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Author(s):

Bertsch, Pascal; Savorani, Laura; Fischer, Peter Alfons

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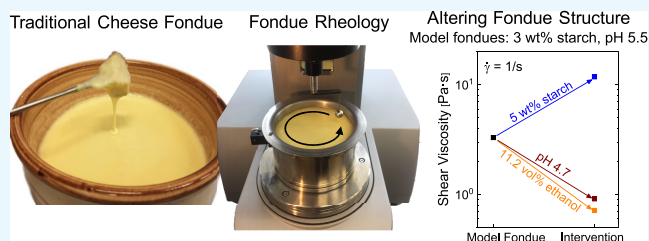
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Rheology of Swiss Cheese Fondue

Pascal Bertsch,^{*} Laura Savorani, and Peter Fischer^{*}

Institute of Food Nutrition and Health, ETH Zurich, Schmelzbergstrasse 7, 8092 Zurich, Switzerland

ABSTRACT: Cheese fondue is a popular Swiss dish prepared by melting cheese under the addition of wine, starch, and seasoning. The flow behavior or rheology of fondue is crucial for mouthfeel, flavor release, and the tendency of fondue to cling to the bread. Fondue is a complex multiphase system whose rheology is determined by the interactions of its colloidal ingredients. We establish cheese fondue as a water-continuous system with dispersed fat droplets, charged caseins, and starch granules. Irreversible phase separation, a common issue in fondue preparation, may be prevented by addition of a critical minimum starch concentration. Fondue was found to be a shear-thinning yield stress fluid, which is desirable for mouthfeel and facilitates fondue to cling to the bread for consumption. Fondue showed a viscoelastic stress response around the gel point ($G' \approx G''$), which is proposed as crucial for the balance of orally perceived gumminess (G') and liquidity (G''). Ethanol addition and lowering pH toward the isoelectric point of casein, as associated with wine addition, decrease fondue viscosity due to a decrease in casein micelle size. Below the isoelectric point of casein, fondue is unstable and phase separates, potentially impeding fondue digestion. Thus, fondue rheology is governed by the complex colloidal interactions within its ingredients, and ultimately determines fondue eating experience.



INTRODUCTION

Cheese fondue is a traditional Swiss dish eaten by dipping pieces of bread in a shared pot. It is prepared by adding wine, starch, and seasoning to melted cheese, making fondue a multiphase system with complex colloidal interactions and rheology.¹ Fondue rheology is of particular importance for mouthfeel, flavor perception, and letting the cheese cling to the bread for consumption. Many half-truths persist in Swiss kitchens on how to prepare the perfect fondue and achieve ideal structure while preventing phase separation. In this study, we assessed the influence of fondue ingredients and their colloidal interactions on the stability and rheology of cheese fondue.

Most hard cheeses are produced by rennet-induced casein coagulation. The decreased steric and electrostatic repulsion results in the aggregation of caseins into clusters and chains.^{2–4} In its solid state, cheese can be considered a two-phase-filled gel with fat globules entrapped in a continuous casein network.^{5–7} The melting behavior of cheese depends on several superimposed factors. At room temperature, approximately 50% of the fat is in its solid state. At 40 °C, the fat is fully liquid and acts as a plasticizer within casein micelles.^{8,9} The casein network shrinks with increasing temperature and water is expelled because of increased hydrophobic interactions. This leads to a decrease in viscosity and finally melting.^{10–13}

While the colloidal structure and interactions in milk and solid cheese have been widely investigated, comparably little is known about colloidal interactions in melted cheese. When preparing fondue, about 30–40 wt % of white wine is added, introducing water and ethanol to the melted cheese. The final fondue is a water-continuous colloidal system with dispersed

proteins and emulsified fat droplets. Phase separation of the solid protein, the aqueous, and the lipid phase is a common issue in fondue preparation and is commonly prevented by the addition of starch. It is suggested that the viscosity of fondue depends on the colloidal interactions of these three dispersed ingredients: starch, casein, and fat droplets. Starch is fully gelatinized at the consumption temperature of fondue. It absorbs parts of the water and thickens the fondue by formation of a soft particle suspension.¹⁴ The fat droplets contribute to fondue viscosity by viscous friction.¹⁵ In cheese, casein micelles are no longer intact and rely as aggregated clusters or chains. Upon melting and dispersion in water, the caseins can be considered charged suspended particles. Electrostatic interactions thus increase in importance.^{16–18} The isoelectric point of casein is ≈ 4.7 and may vary due to decarboxylation or deamination reactions during cheese ripening.¹⁹ Above the isoelectric point, casein is negatively charged, resulting in electrostatic repulsion. Lowering pH toward the pI favors casein inter- and intramolecular attractive interactions, resulting in a more compact structure.^{3,20} Because of its surface-active nature, casein will partially adsorb at dispersed oil droplets.¹⁶

Wine addition further introduces ethanol to the fondue. The influence of ethanol on casein has only been investigated in milk. Low concentrations of ethanol decrease casein micelle size and thus viscosity, while concentrations above 10 vol % induce casein aggregation and increase viscosity.^{21,22} As caseins

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already aggregate during rennet-induced coagulation, the influence of ethanol in melted cheese may differ.

The sum of all of these colloidal interactions governs the rheology and ultimately eating experience of cheese fondue. This study tackles the complex multiphase system fondue from a materials science perspective. Fondue ingredients were systematically added to a model fondue made from cheese and water to understand their individual effect. The colloidal interactions within the fondue constituents were assessed by its rheology and implications on fondue eating experience are discussed.

RESULTS AND DISCUSSION

Rheology of Swiss Cheese Fondue: Effect of Starch, Ethanol, and pH. Traditional moitié-moitié model fondues were prepared from Gruyère and Vacherin (1:1) with 40 wt % deionized water, resulting in a total water content of 64 wt %. All thickener and ethanol concentrations are expressed relative to this water content. Irreversible phase separation is a common issue in fondue preparation, commonly prevented by starch addition. Without starch, fondue readily phase separates into a rubbery protein phase, an aqueous phase, and creamed oil because of coalescence and density differences, as depicted in Figure 1. At 2 wt % starch, a protein phase covered by a

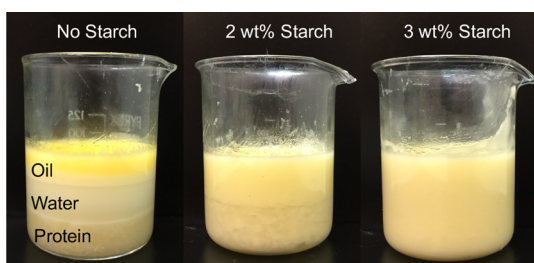


Figure 1. Images of model fondues prepared from melted Gruyère and Vacherin (1:1) and 40 wt % water with different concentrations of potato starch. Pictures were taken 4 h after preparation at room temperature.

stable emulsion without creaming was observed. From 3 wt % starch, no phase separation occurred and a homogeneous fondue was obtained. The starch granules absorb excess water and form a 3D jammed particle suspension.¹⁴ Consequently, a minimum critical starch concentration of 3 wt % is required to prevent fondue phase separation.

The rheology of stable model fondues was assessed by shear and oscillatory rheology. Figure 2A,B depicts flow curve and yield stress experiments of fondues with increasing starch concentrations. All samples showed shear-thinning behavior and had an apparent yield stress. Thus, fondue is a shear-thinning Herschel–Bulkley fluid.²³ Viscosity and apparent yield stress increased with higher starch concentrations. The yield stress corresponds to the minimum stress required to induce flow. With respect to fondue, it could predict the tendency of the fondue to cling to the bread. Also shown in Figure 2A,B is a fondue with 3 wt % starch produced with a model wine (water–ethanol mixture) instead of pure water, introducing 11.2 vol % of ethanol relative to the water content. The addition of ethanol decreased shear viscosity and apparent yield stress. Ethanol is known to reduce casein micelle size and thereby decrease the viscosity of dairy products.²¹ Literature suggest that casein aggregates at ethanol concentrations above

10 vol %, what could increase viscosity.²² This effect is not observed in fondue as casein is already fully aggregated during cheese production.^{5,24}

Oscillatory rheological amplitude and frequency sweeps (Figure 2C,D) revealed that fondue is a viscoelastic fluid around the gel point ($G' \approx G''$ in frequency sweeps).²⁵ Increasing starch concentration enhanced the storage modulus G' and resistance against high stresses. The balance of elastic and viscous properties could be crucial for fondue mouthfeel. Predominantly elastic properties could make the fondue gummy, while in case of dominating viscous properties, the fondue could be perceived too liquidy. The influence of fondue rheology on mouthfeel is discussed in detail later.

Besides starch and ethanol, the fondue structure may be influenced by pH. As casein is a charged protein with isoelectric point $pI = 4.7$, the electrostatic interactions within caseins or within casein and Ca^{2+} strongly depend on pH.^{20,22} The model fondues prepared with water had a pH of 5.5 and casein thus has a negative net charge. The addition of acidic white wine (pH 3–4²⁶) reduces the pH toward pI and decreases casein net charge. Lowering fondue pH from 5.5 to $pI = 4.7$ (from net negative to no net charge) resulted in a decrease in shear viscosity and apparent yield stress (Figure 3A,B). At the point of no net charge, casein no longer possesses a counterion cloud and is in its most compact conformation. This reduces the effective hydrodynamic diameter of casein and thus viscosity.²² This effect was only partially reversible upon charge inversion at pH 3.6 (positive net charge). Shear viscosity and apparent yield stress increased again at pH 3.6 but were still lower compared to pH 5.5, even though the positive net charge would allow a more extended casein structure. This suggests the importance of electrostatic interactions within casein and Ca^{2+} . Without the ionic bridging of negatively charged casein and Ca^{2+} , no continuous protein network can be formed and phase separation is induced, as shown by the image in Figure 3A. The protein forms a rubbery precipitate, associated with a sharp increase in G' at pH 3.6 (Figure 3C,D). In Swiss kitchens, although unknowingly, a low fondue pH is counteracted by the addition of sodium bicarbonate. It is added to increase the airiness of fondue associated with released CO_2 . Our results suggest that fondue creaminess might also be enhanced due to an increase in pH.

As indicated before, little is known about the structure and interactions of casein after cheese melting. We observed a decrease in viscosity upon ethanol addition, in contrast to the increase observed in milk due to casein aggregation.²² This indicates that caseins remain aggregated after cheese melting. The pH-sensitivity of fondue underlines the importance of casein electrostatic interactions after melting. Electrostatic repulsion increases the effective diameter of caseins and results in a more extended form of aggregated casein clusters or chains. The minimum viscosity was observed at the isoelectric point, where casein aggregates are in their most compact conformation. Hence, in melted cheese or fondue, caseins are present as charged suspended aggregates. Decarboxylation or deamination reactions may alter the charge distribution of casein during cheese ripening.¹⁹ However, we did not observe a considerable deviation from the $pI \approx 4.7$.

Rheology is a common method for the characterization of solid cheese or its melting behavior.^{7,10} Ustunol et al.²⁷ found a good correlation of the complex modulus G^* and meltability, allowing to predict cheese melting from rheological experiments. Small amplitude oscillatory shear experiments were

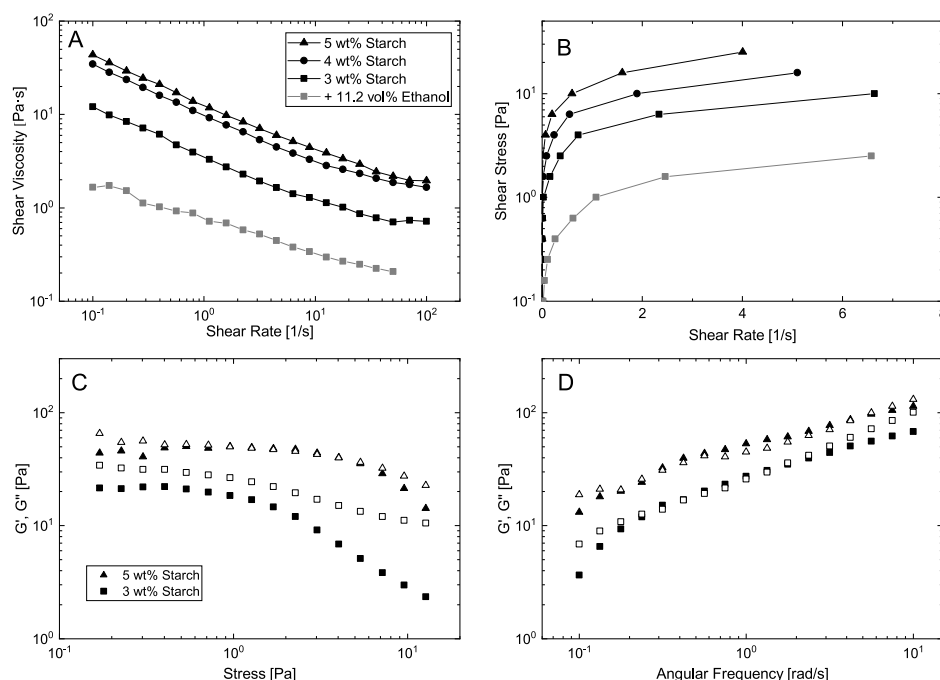


Figure 2. (A) Flow curve and (B) yield stress experiments of model fondues at pH 5.5 with increasing starch concentration and a model fondue with 3 wt % starch and 11.2 vol % ethanol. Oscillatory amplitude (C) and frequency (D) sweep experiments depicting storage modulus G' (full) and loss modulus G'' (empty) at 1 rad/s and 0.1 Pa, respectively. Experiments were performed at 70 °C. Lines are to guide the eye.

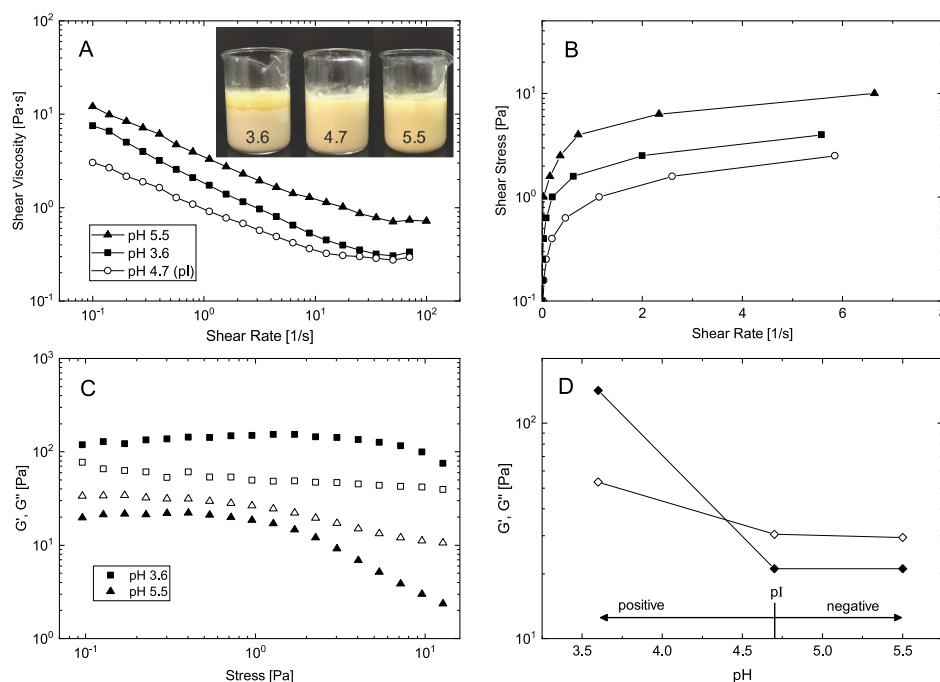


Figure 3. (A) Flow curve and (B) yield stress experiments of model fondues at 3 wt % starch and different pH. The inset in (A) depicts respective model fondues 4 h after preparation. (C) Oscillatory amplitude sweep at 1 rad/s depicting storage modulus G' (full) and loss modulus G'' (empty) for fondues at pH 5.5 and 3.6. (D) Dynamic moduli at 1 rad/s and 0.5 Pa as a function of pH. The isoelectric point ($pI = 4.7$) and respective casein charge are illustrated. Experiments were performed at 70 °C. Lines are to guide the eye.

further established to assess the melting and resolidification of Raclette cheese.²⁸ However, the rheological evaluation of melted cheese is often difficult due to wall slip.^{29,30} The use of a ball measuring system could be a promising alternative to assess the rheology of melted cheese.

We could demonstrate that fondue rheology is governed by the colloidal interactions of starch, casein, and fat droplets.

Being a natural fermented product, cheese composition and final fondue rheology may vary within different batches and cheese varieties. As the colloidal constituents essentially remain the same, we assume that the observed effects of starch, ethanol, and pH are applicable for fondues made from any rennet-coagulated cheese.

Rheology of Swiss Cheese Fondue Stabilized with Xanthan or ι -Carrageenan. Thickening agents are commonly applied in the food industry to stabilize or alter the structure of food. A broad range of food grade thickeners exists, which all show specific rheological characteristics depending on their structure.^{31,32} The addition of a thickening agent to fondue is essential to prevent phase separation, as discussed before. However, traditional starch may be replaced. Two alternative thickening agents commonly used in foods, negatively charged ι -carrageenan and branched xanthan gum, were investigated.

Both alternative thickeners were able to prevent phase separation at factor ≈ 10 lower concentrations compared to starch (Figure 4). This derives from their different structures

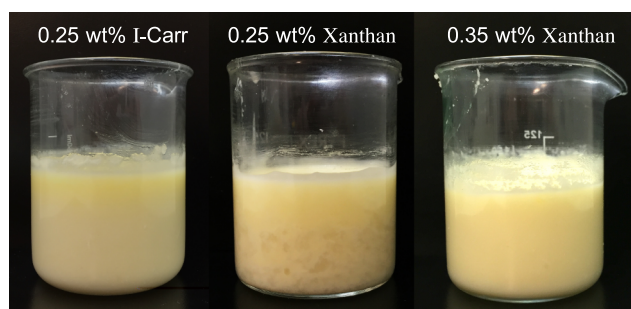


Figure 4. Images of model fondues prepared from melted Gruyère and Vacherin (1:1) and 40 wt % water with different concentrations of ι -carrageenan and xanthan gum. Pictures were taken 4 h after preparation at room temperature.

and thickening mechanisms. While starch forms a granular suspension, ι -carrageenan and xanthan have an elongated fibrous structure,³¹ resulting in significantly lower critical overlap concentrations. ι -Carrageenan was the most efficient

thickener for fondue. Only minor creaming was observed at 0.25 wt % in contrast to protein precipitation with xanthan. Negatively charged ι -carrageenan is known to interact with Ca^{2+} and positively charged casein, making it an efficient stabilizer of dairy products even at low concentrations.³³

Figure 5A,B depicts the flow curves of fondues stabilized with xanthan and ι -carrageenan, respectively. Compared to starch, the flow curves had a steeper slope. The viscosity was higher at low shear rates but similar or even lower at high shear rates. This again derives from the fibrous structure of xanthan and ι -carrageenan. At rest, they form an interconnected network, while at increasing shear rate, they align in the flow field. The fibrous thickeners further resulted in a significantly higher apparent yield stress (Figure 5C). Xanthan is known to have a high yield stress because of its fibrous branched structure.³⁴ In the case of linear ι -carrageenan, the yield stress might be increased by electrostatic interactions with casein and Ca^{2+} .³³ Figure 5D depicts G' and G'' as a function of thickener concentration. For fibrous xanthan and ι -carrageenan, G' was higher than G'' at all employed concentrations. For starch, lower values were observed and G'' was still predominant at low starch concentrations. It was argued before that the characteristic viscoelastic response around the gel point could be crucial for fondue oral perception. Thus, the rheological behavior of fondue can be altered by the addition of alternative thickeners. However, too high concentrations of fibrous thickening agents could make fondue too thick or gummy.

Implications on Fondue Eating Experience. Cheese fondue is an excellent example of a complex food system whose eating experience is governed by its rheology. The yield stress of fondue is crucial as the cheese needs to properly coat the bread and resist gravity. The thickness of the cheese layer probably increases with viscosity. Traditionally, losing a piece of bread in the fondue is punished according to premeal

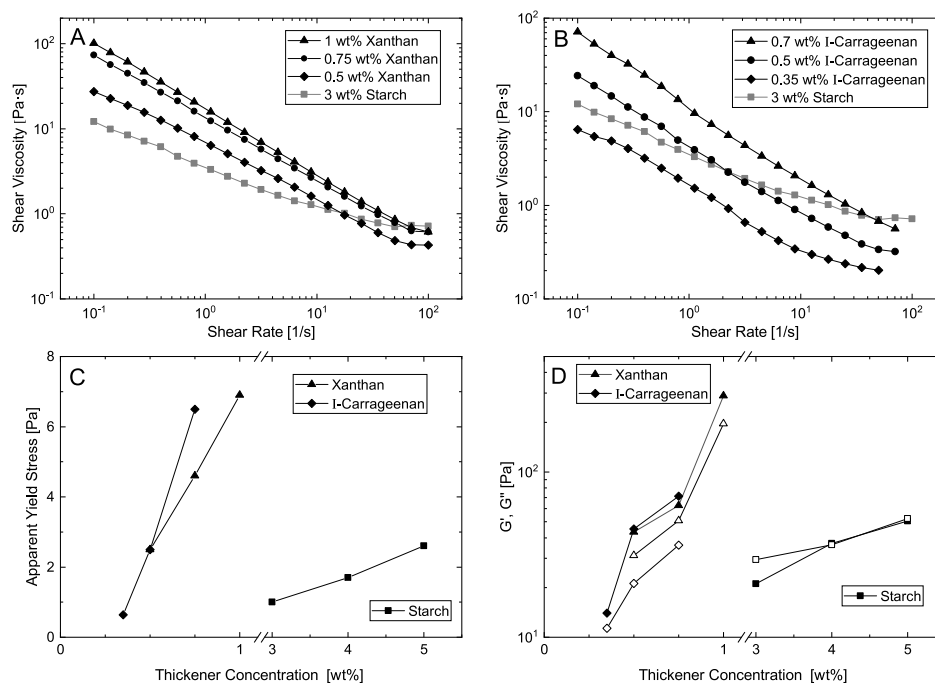


Figure 5. Flow curves of model fondues stabilized with xanthan (A) and ι -carrageenan (B). Fondues with 3 wt % starch (gray) are shown for comparison. (C) Apparent yield stress as a function of different thickener concentrations. (D) Storage modulus G' (full) and loss modulus G'' (empty) at 1 rad/s and 0.5 Pa as a function of different thickener concentrations. Experiments were performed at 70 °C. Lines are to guide the eye.

consensus of all participants, a risk that could be increased by a high yield stress.

The rheology of food further governs its oral perception. The shear-thinning behavior of fondue could be desirable during oral processing and enhance flavor release. Orally perceived thickness correlates with viscosity, whereas flavor release correlates inversely with viscosity.^{35,36} On the other hand, a high viscosity increases oral coating associated with prolonged flavor perception.³⁷ Fondue was found to be a viscoelastic fluid around the gel point. We proposed that this viscoelasticity is crucial for fondue texture perception. Upon increasing elastic properties, for example, by addition of excess starch, a fondue could be perceived too gummy. On the other hand, a predominantly viscous fondue, for example, due to excess wine, could lose its yield stress and be perceived too liquidly. Guggisberg et al.²⁸ could previously link the rheology of Raclette cheese, another typical Swiss dish, to its sensory perception.

The irreversible phase separation of fondue is a common issue and has ruined countless dinners. It may be avoided by sufficient addition of water-binding thickeners, for example, 3 wt % starch relative to the total water content. Traditional starch may be replaced by alternative thickeners like ι -carrageenan or xanthan, allowing us to alter fondue rheology depending on the structure and electrostatic interactions of the employed thickener. We are aware that this will hardly be acknowledged by Swiss people for future fondue preparation. However, we consider this an alternative for the dairy industry and an interesting case study on how different thickening agents behave in a complex multiphase system like fondue.

The acid instability of fondue could have implications on its digestibility. Everyone who ever had fondue can testify that fondue digestion may be a long-lasting process. Upon ingestion, fondue is mixed with gastric fluids. High-viscosity meals generally impede gastric mixing and increase perceived fullness.³⁸ We observed phase separation upon decreasing pH below the isoelectric point of casein (4.7), suggesting that fondue phase separates under gastric conditions. Gastric unstable emulsions are associated with delayed gastric fat emptying due to fat layering in the upper stomach. This impedes fat sensing and digestion which occurs in the duodenum, resulting in delayed satiation.^{39,40} Further, fondue gelled upon acidification. The gastric gelling of emulsions can significantly reduce the release and digestion of fat.^{41,42} A delayed but tremendous feeling of fullness is indeed often experienced after fondue consumption. In Switzerland, there is a never-ending dispute about the correct beverage to be consumed with fondue, as alcoholic beverages are proclaimed to ease fondue digestion.⁴³ Heinrich et al.⁴⁴ could show that the opposite is the case. Alcohol induces gastric relaxation and might provide short-term relief. However, fat emptying and digestion are delayed, promoting long-term postprandial fullness.

CONCLUSIONS

Cheese fondue is a popular Swiss dish made from melted cheese, wine, and starch. There is no bigger shame in Switzerland than serving a fondue that is too liquid, gummy, or even phase-separated, and many myths without scientific base persist in Swiss kitchens on how to prepare the perfect fondue. This study assessed the most relevant colloidal interactions and their influence on stability and rheology of model fondues.

Fondue can be considered a water-continuous system with dispersed fat droplets, caseins, and starch. The caseins remain aggregated after melting and are governed by pH-dependent electrostatic interactions. A minimum critical starch concentration of 3 wt % is required to form a jammed soft particle suspension and prevent phase separation. About 10-fold lower concentrations may be employed in the case of more elongated, fibrous thickeners. Negatively charged ι -carrageenan was found to be most efficient because of electrostatic interactions with casein and Ca^{2+} . The elongated thickening agents resulted in increased elastic properties, higher apparent yield stress, and more pronounced shear thinning.

Fondue is a shear-thinning yield stress fluid around the gel point ($G' \approx G''$). The shear-thinning behavior is desirable for oral processing and mouth feel, while a yield stress is essential to make the fondue cling to the bread for consumption. We argued that the characteristic viscoelastic response around the gel point ($G' \approx G''$) is crucial for fondue oral perception, as fondue may be perceived too gummy ($G' \gg G''$) or too liquidly ($G' \ll G''$). Lowering pH and the presence of ethanol both result in a more compact casein structure and decreased viscosity. Consequently, wine addition reduces fondue viscosity. Below the isoelectric point of casein, fondue is unstable and phase separates, potentially delaying fat digestion. Hence, the eating experience of cheese fondue is governed by its complex colloidal interactions and resulting rheology.

EXPERIMENTAL SECTION

Materials. The cheeses (Gruyère and Vacherin) were kindly provided by Emmi Fondue AG (Langnau i. E., Switzerland). Potato starch was obtained from Emsland Group (Emlichheim, Germany), and HCl (37% fuming) was obtained from Merck (Buchs, Switzerland). Xanthan gum was purchased from Jungbunzlauer (Basel, Switzerland), and ι -carrageenan was purchased from Sigma-Aldrich (Schaffhausen, Switzerland).

Model Fondue Preparation. A traditional moitié-moitié (50% Gruyère, 50% Vacherin) fondue was prepared from 60 wt % cheese and 40 wt % deionized water. Taking the water content of the cheeses (from product specifications) into account, the final water content of model fondues was 64 wt %. All thickener and ethanol concentrations specified in the manuscript are expressed relative to this water content. The thickening agents were suspended in deionized water and heated to 70 °C under stirring. Grated Gruyère and Vacherin were added under stirring until a homogeneous fondue was obtained. Measurements were performed at 70 °C. The temperature dependence of model fondues is provided in Figure 6. The native pH of the model fondues was 5.5 and was adjusted by addition of 1 M HCl solution.

Steady Shear Rheology. Shear rheology experiments were performed with an Anton Paar MCR 302 (Graz, Austria) equipped with a ball measuring system (BMS) 2 with a diameter of 12 mm.⁴⁵ The fondue was transferred to the preheated measuring cup and a transient measurement at a shear rate of 10 s⁻¹ was performed until temperature and shear viscosity were constant. Fondue flow curves were assessed by increasing the shear rate from 0.1 to 100 s⁻¹. The apparent yield stress was determined by increasing shear stress until flow was induced. The temperature was controlled by a water bath via the double jacketed cup and determined with a Pt₁₀₀ temperature sensor (Anton Paar) immersed in the fondue. The cup was covered with a home-made PVC solvent trap.

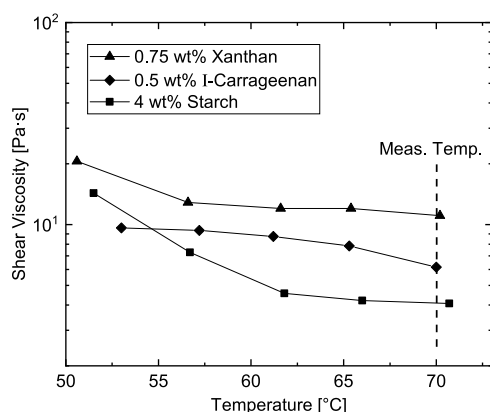


Figure 6. Shear viscosity at measured at 1 s^{-1} as a function of temperature of fondues prepared with different thickening agents. Lines are to guide the eye.

Oscillatory Rheology. Oscillatory rheology was performed with a dynamic stress rheometer (DSR) (Rheometric Scientific GmbH, München, Germany) using a Couette geometry (32 mm cup diameter, 29 mm bob diameter, and 44 mm bob length). Amplitude sweeps were performed at 1 rad/s and frequency sweeps at 0.1 Pa . The temperature was controlled by a water bath.

AUTHOR INFORMATION

Corresponding Authors

*E-mail: pascal.bertsch@hest.ethz.ch. Phone: +41 44 632 67 62 (P.B.).

*E-mail: peter.fischer@hest.ethz.ch (P.F.).

ORCID

Pascal Bertsch: 0000-0002-9188-2912

Peter Fischer: 0000-0002-2992-5037

Notes

The authors declare no competing financial interest.

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