Time dependence in jamming and unjamming

Promotor:

Prof. dr. E. van der Linden
Hoogleraar in de fysica en fysische chemie van levensmiddelen
Wageningen Universiteit

Promotiecommissie:

Prof. dr. ir. F.A.M. Leermakers, Wageningen Universiteit
Dr. T. Nicolai, Université Du Maine, Le Mans, Frankrijk
Prof. Dr. C. Baravian, École Nationale Supérieure d'Electricité et de Mécanique, Vandœvre lès Nancy, Frankrijk
Prof. Dr. C.G. de Kruif, Universiteit Utrecht

Dit onderzoek is uitgevoerd binnen de onderzoekschool VLAG

Time dependence in jamming and unjamming

Alan Parker

Proefschrift
ter verkrijging van de graad van doctor
op gezag van de rector magnificus
van Wageningen Universiteit,
prof. dr. M.J. Kropff
in het openbaar te verdedigen
op dinsdag 30 juni 2009
des namiddags om 16:00 uur in de Aula

ISBN: 978-90-8585-387-9

Alan Parker (2009)

Time dependence in jamming and unjamming

PhD thesis, Wageningen University, The Netherlands

Keywords: Jamming, aging, spin glass, gel, rheology, thixotropy, sedimentation, depletion flocculation, emulsion, gelatin, carrageenan

Abstract

Three different food systems have been studied: emulsion/polymer mixtures, gelatin gels and carrageenan gels. Typically, samples are trapped, or jammed, far from equilibrium. The simple jamming paradigm suggests that, once in the jammed state, these systems are static. This useful approximation is often too simple, since these systems frequently evolve in time. Their evolution has been measured systematically. Where possible, these results have been placed in the context of the physics of out-of-equilibrium systems.

The emulsion/polymer mixtures are a model for salad dressing. The emulsions alone are colloidally stable, but become inhomogeneous, due to the effects of gravity. With sufficient polymer, they can be apparently stable (jammed) for months, but then quite suddenly start to sediment – the system unjams. The kinetics of this delayed sedimentation is measured as a function of the key parameters. A new model is proposed for the mechanism by which polymers stabilize emulsions.

Solutions of gelatin gel when cooled, due to the formation of portions of helix. A new model relating the amount of helix to the elasticity is described. The gels always evolve slowly. At steady state, the rate of evolution of the elasticity is constant in log(time), so this system conforms to Struick’s physical aging scenario. The effect of temperature changes on the evolution of gels is extremely complex. The results show that there is a deep analogy between this behavior and that of spin glasses, which are exotic magnetic phases.

Gels of iota carrageenan, a seaweed polysaccharide, have unique rheological properties: they regel almost instantly after strong mixing. This property is used in the dairy industry, but has not been studied previously. The kinetics of recovery after shear has been measured for water gels and milk gels.

Table of contents

Chapter 1 Introduction 1

Chapter 2 How does xanthan stabilise salad dressing? 9

Chapter 3 Delayed sedimentation as a paradigm for formulating gravitationally stable dispersions 25

Chapter 4 Elasticity Due to Semiflexible Protein Assemblies near the Critical Gel Concentration and Beyond 45

Chapter 5 Scaling in the dynamics of gelatin gels 53

Chapter 6 Spin glass-like dynamics of gelatin gels 65

Chapter 7 Thixotropic gels and dairy desserts 75

Chapter 8 Discussion and Conclusions 89

Acknowledgements 95

Curriculum vitae 97

List of publications 98

Chapter 1

Introduction

“A scientist is supposed to have a complete and thorough knowledge, at first hand, of some subjects and, therefore, is usually expected not to write on any topic of which he is not a master. This is regarded as a matter of noblesse oblige. For the present purpose I beg to renounce the noblesse, if any, and to be freed of the ensuing obligation. My excuse is as follows: We have inherited from our forefathers the keen longing for unified, all-embracing knowledge. From antiquity and throughout many centuries the universal aspect has been the only one to be given full credit. But the spread, both in width and depth, of the multifarious branches of knowledge has confronted us with a queer dilemma. We feel clearly that we are only now beginning to acquire reliable material for welding together the sum total of all that is known into a whole; but, on the other hand, it has become next to impossible for a single mind fully to command more than a small specialized portion of it. I can see no other escape from this dilemma (lest our true aim be lost forever) than that some of us should venture to embark on a synthesis of facts and theories, albeit with second-hand and incomplete knowledge of some of them - and at the risk of making fools of ourselves.”

Erwin Schrödinger, “What is life?” (1944)

The science recounted here is far from the grandeur of Schrödinger's project, but I share the same desire for the synthesis of areas, some of which I do not fully understand. So I request the same indulgence for the same reason: trying to make new connections between different scientific disciplines is a risky business.

This thesis is in food science. Food science is concerned with understanding food. Economic forces are strong drivers of the subject. Consumers have paradoxical, and mutually incompatible, desires. They want their food to be: i) cheap, ii) nutritious, iii) stable for a long time, iv) easy to prepare, v) look and taste as good as if it has just been prepared in a traditional way, vi) free from additives, allergens, genetically modified organisms, etc, vii) respectful of cultural and religious norms: vegetarian, halal, kosher, etc. Due to the strong emotions that food generates, consumers have difficulty coping with the idea that all of these constraints cannot be satisfied simultaneously. The scientific study of food helps industrialists to achieve these goals.

Food science is applied: it uses ideas from other areas to improve our understanding of the food we eat. All of the systems studied here are everyday foods. By digging deeply to understand the practical problems presented by these foods, I have discovered interesting new connections. Some of them turn out to be new science. The idea that everyday phenomena can inspire real science, and future scientists, has become popular among academic physicists in recent years. Sydney Nagel has discussed "Physics at the breakfast table" [1]; Tom Witten has explained coffee rings [2]; Christophe Clanet can get a paper entitled "On the glug-glug of ideal bottles" [3] published in the prestigious Journal of Fluid Mechanics. Fortunately, the days when Nobel-Prize winner Murray Gell-Mann could think that calling solid-state physics "Squalid state physics" [4] was amusing are far behind us.

These examples show that we should be careful not to confuse playfulness with bad science. Sir Michael Berry won the IgNobel prize for his (correct) theory of how to levitate a frog with a magnetic field [5]. The result is mathematical physics of the highest order. I do not claim to be a scientist like those just mentioned. They use everyday phenomena as vehicles to explain science. I am paid to understand everyday phenomena and need science to do it. On a spectrum from the production manager of a sweet factory to an academic physicist, I sit somewhere in the middle. Unlike academic physicists, I know how factories work and what the problems are. Unlike production engineers I seek to use the latest physics to solve them.

The theme unifying this thesis is "jamming"; in the sense of traffic jams. The origin of the word is obscure, but it may come from the Arabic "jāmid", meaning "congealed". A native speaker told me that the word is used to describe over-fermented yoghurt. About ten years ago, the word was hijacked by physicists to express the sudden slowing down of systems far from equilibrium [6]. The three systems studied here are very diverse, but they share this characteristic. Unjamming is simply the reverse of jamming: a jammed system starts to move again, usually because it has been heated or agitated.

In everyday life, we often observe that things get stuck for no apparent reason. As the density of traffic increases, it flows fast, then flows slowly and finally stops completely. Powder flowing in pipes suddenly blocks. Banging the pipe will usually unblock it. In 1997, a group of physicists decided to see how far they could unite these diverse phenomena under a single theoretical umbrella [7]. Their central intuition was that the characteristics unifying jammed systems are independent of many details, for instance the size of its constituents. Instead, these systems are controlled by other characteristics; for example the free volume: the amount of space that each entity has to move in. They were not certain of success, but thought that, at worst, they would have achieved a noble failure. The immediate result was a useful book of reprints and review articles [7]. As well as traffic and powder (also called granular media) they hoped to include glasses, like window glass and colloidal dispersions, like mayonnaise. So their ambition stretched from molecular fluids to colloidal dispersions to sub-millimeter powders to cars.

When the word “jam” is mentioned in everyday conversation, two things come to mind: fruit jam and traffic jams. In a pleasing conjunction, this thesis is concerned with both senses. The jammed systems that are studied are all gels. Two are molecular and one is colloidal.

Gels are semi-solids trapped far from equilibrium. Understanding them is difficult, because their behavior cannot be explained using concepts from standard equilibrium physics. They are very common in food. Any food that you can imagine between the extremes of drinks (usually low viscosity, unstructured liquids) and crunchy solids (glasses) is likely to be a gel.

A simple and helpful way to start thinking about gels is to assume that time has no importance: once a system has gelled, it is stuck and nothing else happens. This assumption is at the heart of the jamming paradigm [6]: systems are either jammed or not jammed. There is a very clear change in state: the system suddenly stops. However, the microscopic changes underlying this sudden macroscopic change are surprisingly elusive. Trappe and Weitz [8] extended the original jamming paradigm to construct a “universal” jamming phase diagram for colloidal gels. They assumed that three dimensionless parameters control the system: the particle volume fraction, the particle stickiness and the applied stress. The particle stickiness is made dimensionless by dividing by thermal energy (k_BT). In statistical physics jargon, this number is called the system temperature. It is distinct from the temperature measured with a thermometer. The stress is made dimensionless by dividing by the thermal energy density (k_BT/R^3). This simple picture is very helpful as a “sketch map” to start understanding colloidal gels.

In reality, the simple assumption that a system either is or is not in the jammed state has its limits. In particular, it breaks down close to the jammed/unjammed frontier. Here, time matters and the systems are clearly evolving. Studying and trying to understand this evolution is the theme that unites the three parts of this thesis.

Systems studied

I have studied three very different systems:

i. Emulsion/polymer mixtures: Oil-in-water emulsions are common in food, e.g. Mayonnaise, salad dressing and ice cream. Commercial salad dressing must have a long shelf life, i.e. retain an unchanged appearance for a long time. The addition of polymer thickener is vital to prevent gravitational separation, which is perceived as a loss of quality.

ii. Gelatin gels are the classic thermoreversible gels, irreplaceable in foods like the jelly babies/gummy bears. Gelatin is an animal protein, derived from collagen [9].

iii. Iota carrageenan is a seaweed polysaccharide. It forms weak, transparent gels with and without milk. They have the fascinating property of almost instant mechanical reversibility. Several papers on my publication list, but not included here, are concerned with the iota carrageenan: its interactions with milk, modeling its thixotropy [10] and determining its purity, without expensive analytical methods [11].

Key concepts

A number of concepts form a map of the area of science that this thesis covers. Most of them are ordinary words that have been given a special meaning. Here is an alphabetical list with a brief description of each.

Aging: In physics "aging" or "physical aging" refers to the slow hardening of systems. As time passes, the system gets harder: the same stimulus (mechanical, magnetic, etc.) causes a smaller response; also the rate of hardening decreases. Often the rate is roughly proportional to log(time since preparation). Aging was first described in glassy polymers by the Dutch polymer scientist Struick [12]. Since then it has been found in a wide range of systems [13].

Ergodicity: a system is ergodic when there is equivalence between its average properties when measured i) at one place over a long time and ii) at many places over a short time; so the averages over time and space are equal. Systems in thermal equilibrium are ergodic. Metastable systems trapped out of equilibrium are not. In a key paper, Bouchaud [14] argued that aging is a consequence of "weak ergodicity breaking" (WEB). A strongly non-ergodic system is broken up into many completely separate systems. In the WEB scenario, one separate metastable state can be reached from another *occasionally*, leading to slow dynamics characterized by aging and intermittency. This scenario is exactly what is needed to fit in between the unjammed (ergodic) and totally jammed (completely non-ergodic) states. Experimentally, we can check if a system is ergodic or not by using dynamic light scattering. If the correlation function falls to zero, then the system is ergodic, since the correlations between different parts of the system fall to zero.

Frustration: a physical system is said to be frustrated when it is impossible for two different constraints to be satisfied simultaneously. Think about people leaving a crowded building that is on fire. Everyone rushes to the exit. Usually this causes the exit to block almost completely. The system is frustrated because the individual wish to get out as fast as possible is incompatible with the best global way to empty the building: forming orderly queues. This conflict between global optimization and local optimization is a key characteristic of all jammed systems [15].

Intermittency: thermally equilibrated systems have continuous dynamics. Thermal kicks with a Gaussian distribution cause the systems to fluctuate about an average state or to move smoothly between equilibrium states. When a system is frustrated, this is no longer true. The system can get trapped in a metastable state. Only a kick bigger than any previous ones (called a "record breaker" by Sibani [16]) can cause it to evolve, so, most of the time, the system looks stable, with its activity confined to intermittent, violent bursts ("quakes", "avalanches"). Intermittency can be measured using either noise measurements [17] or by scattering techniques with high temporo-spatial resolution [18]. These techniques are at the leading edge of experimental physics and they have not been applied the systems described here. I predict that this simple picture of intermittent dynamics will apply to the systems studied here. Recent developments in light scattering make this prediction testable [18].

Jamming/Unjamming: "Jamming" is a concept that seeks to unify a range of systems that are trapped far from equilibrium. It was originally applied to molecular glasses (like window glass), powders and traffic [7]. It was soon extended to apply to colloids [8].

Percolation: a theory of physics and mathematics that relates the number of bonds in a lattice to its conductivity [19]. For example: Take a square metal net with electrodes along two opposing edges. How does the conductivity between the electrodes change as we cut links at random? What fraction of the links must we cut to be sure that the conductivity will be zero? Surprisingly this kind of question turns up in many diverse areas of science, including flow through porous media (vital for oil production) and fracture. In chapter 4, it is used to relate the concentration of gelatin helices to their elasticity.

Spin glasses: spin glasses are exotic magnetic systems that only exist in certain metallic alloys at temperatures close to absolute zero. They are metastable and exhibit a range of interesting memory effects, including aging [20]. They have no known applications, yet they have been studied very intensely. In fact, most of the work has been on mathematical models of spin glasses. The attraction of such models for theorists is the combination of their mathematical simplicity coupled with highly complex behaviour, which is relevant to many unexpected areas of areas of science, such as memory storage in the brain [21] and difficult optimization problems [22].We should be careful to distinguish between a) work on the mathematical models, which have a life of their own, and b) work on real spin glasses.

Thixotropy: thixotropy is a rheological term [23]. It has been used in several ways. A strict rheological definition is: reversible stress-induced changes in viscosity, where higher stress induces lower viscosity. In this sense it can only be a property of reversible systems. A less strict definition is to qualify a sample as thixotropic if it recovers, at least partially, some of its initial structure after shearing. In this broader sense, we call samples "thixotropic" when they are, at least partially, mechanically reversible. A precise definition of thixotropy is likely to remain elusive, as it is clearly present in systems showing both aging and the yield stress. The latter concept alone has generated controversy amongst rheologists for many years [24]. Another important point is that whether a system is called thixotropic depends on the time scale. If the viscosity changes "instantly" when the shear rate or shear stress increases, then rheologists call it "shear-thinning". The definition of "instantly" depends on the rapidity of the measurement technique. One of my publications, not included here, takes a general approach to modeling thixotropy, treating it as a problem in system identification [25]. We seek the simplest set of equations that correctly describe the behavior. This approach is coupled with the use of structural models for the rheology [10].

Overview

Chapters 2 and 3 are studies of the sedimentation of emulsion/polymer mixtures. I was concerned that existing models for the mode of action of the polysaccharide thickener xanthan in “stabilizing” these mixtures were incorrect. In particular, it was suggested that adding xanthan would cause permanent jamming, due to the presence of a yield stress. Further, it was alleged that this yield stress was already present in the xanthan solutions, which have special “weak gel” properties [26]. I was sure that xanthan solutions do not have a yield stress at the concentrations used in salad dressing. Also, I knew that technologists spend vast amounts of time doing “shelf life testing” to determine for how long their formulations are gravitationally stable. I trust these people not waste their time, so the explanation that xanthan addition induced permanent stability had to be wrong. Chapter 2 [27] is a study that aimed to establish a better explanation. We discovered a new phenomenon: delayed creaming and suggested that it could be the basis for rational tests for the gravitational stability of emulsion/polymer mixtures. Chapter 3 is a review of delayed sedimentation, written 14 years after chapter 2. As well as reviewing progress in the general literature, it presents new data on the effects of polymer type and on the effect of centrifugation = gravitational stress and finally suggests elements for the elusive theory needed to explain delayed sedimentation.

Chapters 4 to 6 are concerned with gelatin gels. Chapter 4 [28] presents a novel model for the elasticity of gelatin gels, based on the helix amount. It extends that proposed by Joly-Duhamel et al. [29], whose work caused a key paradigm shift in understanding gelatin gels. Their insight is that the elasticity of gelatin gels is due to interactions between the helical rods, and not to the rubber elasticity of the non-helical coils, as was previously thought. This new model turned out to be the key to providing a plausible explanation for the following work. Chapter 5 [30] is a mainly phenomenological study of the complex memory effects in gelatin gels. It establishes that gelatin gels undergo physical aging. Chapter 6 presents an analogy between gelatin gels and spin glasses. It places the observations of chapter 5 firmly in the context of the contemporary physics of out-of-equilibrium systems.

Chapter 7 is concerned with the remarkable rheological properties of iota carrageenan gels [31]. In the food industry, it is mainly used in dairy desserts, due to carrageenan’s strong interaction with milk protein [32]. Gels of iota carrageenan have unique properties [10]. They are both mechanically and thermally reversible. Despite their widespread use in the food industry and their fascinating properties, they have been little studied. In fact, the paper remains the only one addressing the fast recovery of these gels after breakdown by shear.

References

1. S. Nagel, Am. J. Phys. **67,** 25 (1999).

2. Y. O. Popov and T. A. Witten, Phys. Rev. E **68,** 036306-036306/19 (2003).

3. C. Clanet and G. Searby, J. Fluid Mech. **510,** 145 (2004).

4 . J. Gleick, *Chaos*, Penguin, London 233 (2000).

5. M. V. Berry and A. K. Geim, Eur. J. Phys. **18,** 307 (1997).

6. A. J. Liu and S. R. Nagel, Nature **396,** 21 (1998).

7. A. J. Liu and S. R. Nagel (eds.), *Jamming and rheology: Constrained dynamics on microscopic and mesoscopic scales,* Taylor and Francis, London and New York (2001).

8. V. Trappe *et al.*, Nature **411,** 772 (2001).

9. T. R. Keenan in *Kirk-Othmer Encycl. Chem. Technol. (5th Ed.)*, 12 ed., 2005), 436.

10. C. Baravian, D. Quemada, and A. Parker, J. Texture Studies **27,** 371 (1996).

11. A. Parker in *Food Macromolecules and Colloids*, Royal Society of Chemistry, 495 (1995).

12. L. C. E. Struik, *Physical Aging in Amorphous Polymers and Other Materials*, Elsevier, New York and Amsterdam, 242 (1978).

13. J. P. Bouchaud, L. Cugliandolo, J. Kurchan, and M. Mézard, in *Spin-glasses and random fields*, Edited by A. P. Young, World Scientific, Singapore (1998).

14. J. P. Bouchaud, J. Phys. I France **2,** 1705 (1992).

15. P. E. Anderson, H. J. Jensen, L. P. Oliveira, and P. Sibani, Complexity **10,** 49 (2004).

16. P. Sibani and H. J. Jensen, Europhys. Lett. **69,** 563 (2005).

17. L. Bellon *et al.*, Lect. Notes Phys. **688,** 23 (2006).

18. L. Cipelletti *et al.*, J. Phys.: Condens. Matter **15,** S257-S262 (2003).

19. M. Sahimi, *Applications of percolation theory,* Taylor and Francis, London and New York (1994).

20. E. Vincent, Lect. Notes Phys. **716,** 7 (2007).

21. J. J. Hopfield, Proc. Nat. Acad. Sci. USA **79,** 2554 (1982).

22. S. Kirkpatrick, C. D. Gelatt Jr., and M. P. Vecchi, Science **220,** 671 (1983).

23. J. Mewis and N. J. Wagner, Adv. Coll. Inter. Sci. **147-148,** 214 (2009).

24. H. A. Barnes, Appl. Rheol. **9,** 262 (1999).

25. L. Ljung, *System Identification - Theory For the User*, Prentice Hall, New Jersey, USA (1999).

26. S. B. Ross-Murphy and K. P. Shatwell, Biorheology **30,** 217 (1993).

27. A. Parker, P. A. Gunning, K. Ng, and M. M. Robins, Food Hydrocolloids **9,** 333 (1995).

28. E. van der Linden and A. Parker, Langmuir **21,** 9792 (2005).

29. C. Joly-Duhamel, D. Hellio, A. Ajdari, and M. Djabourov, Langmuir **18,** 7158 (2002).

30. V. Normand and A. Parker in *Proc. 3rd Int. Symp. Food Rheol. Structure*, eds. P. Fischer, I. Marti and E.J. Windhab, 185 (2003).

31. L. Piculell, Food Sci. Technol. **160,** 239 (2006).

32. V. Langendorff *et al.*, Food Hydrocolloids **14,** 273 (2000).

Chapter 2

How does xanthan stabilise salad dressing?

The creaming behaviour of model pourable salad dressings has been studied over a wide range of xanthan and oil phase concentrations. They were produced by mixing a colloidally stable emulsion with xanthan solutions. The model dressings were completely flocculated by depletion at all xanthan concentrations above 0.1g/L. Creaming behaviour was in three phases: an initial delay phase, followed by linear creaming and finally cream compression. Delayed creaming has not been reported previously. It is of great practical interest, because a complete absence of creaming is the aim of successful dressing formulation. The length of the delay phase was proportional to the emulsion concentration, inversely proportional to the oil/aqueous phase density difference and scaled with the xanthan concentration to powers between 3 and 4 over more than four orders of magnitude. Traditionally, the stabilisation of salad dressing by xanthan is explained by the yield stress of its solutions. It is shown that they do not have one, at the appropriate concentrations, and we offer an alternative explanation. It is suggested that dressing stabilisation is due to the particle network which the addition of xanthan induces by depletion flocculation of the emulsion droplets.

A. Parker, P. Gunning, K. Ng and M. Robins, Food Hydrocolloids, **9**, 333, (1995)

Introduction

One of the largest applications of the microbial polysaccharide xanthan is the thickening of pourable salad dressings. In such products, the xanthan serves to prevent creaming, which is an easily identified defect. In the food industry, this effect is often called “stabilisation”, and we will use the term in this sense here. Food technologists explain the use of xanthan to stabilise salad dressings in terms of the high yield stress of its solutions. In this traditional model, the yield stress of the xanthan solution is conferred on the dressing. The emulsion droplets do not cream since the gravitational lift on the droplets is less than the yield stress of the aqueous phase. This explanation is incorrect, since it is easy to demonstrate that xanthan solutions at the concentrations used in salad dressings do not have a yield stress. The way in which this misunderstanding has arisen is illustrated below.

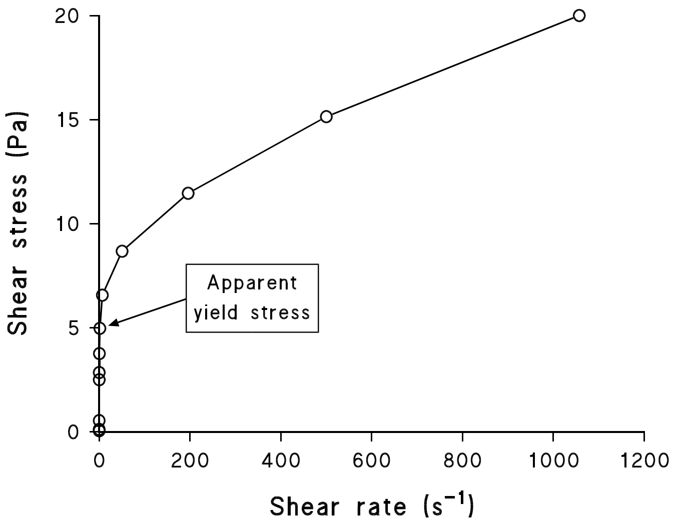

Fig. 1 Flow curve of 5g/L xanthan solution in 1M NaCl and 0.3M acetic acid. Shear stress as a function of shear rate on linear axes.

Figure 1 shows the flow curve of a xanthan solution at a concentration typical of pourable dressings (5g/L). It is in the usual form of shear stress as a function of shear rate on linear axes. It is “obvious” that the xanthan solution has a high yield stress. However, the determination [1], and indeed the existence [2], of the yield stress is a subject of debate. Cheng’s review [1] is a clear, pragmatic explanation of the problem. In summary, the yield stress found depends on the timescale of the measurement, which should correspond to that of the application. For the creaming of salad dressings, the correct timescale is the shelflife of the product, from six months to a year. Even taking this pragmatic point of view, the xanthan rheology shown in figure 1 does not exhibit a yield stress.

Figure 2 demonstrates this point. It shows the same data plotted as log viscosity versus log shear rate. It is now clear that the flow curve tends towards a Newtonian plateau at the low shear rates typical of the timescale of the shelflife. This behaviour is incompatible with the existence of a yield stress, for which the viscosity must tend to infinity at low shear rates, not a plateau [3]. In a recent study, Giboreau et al [4] have come to the same conclusion, but for a xanthan solution at an even higher concentration (8g/L). The dashed line in figure 2 shows a hypothetical flow-curve which would indicate the presence of a true yield stress. We therefore conclude that the conventional explanation of dressing stabilisation in terms of the rheology of xanthan solutions cannot be correct. If salad dressings simply adopted the rheology of their aqueous phases, they would start to cream immediately, although slowly. Yet experience shows that this is not the case, no visible creaming occurs over the shelflife of a well-formulated dressing.

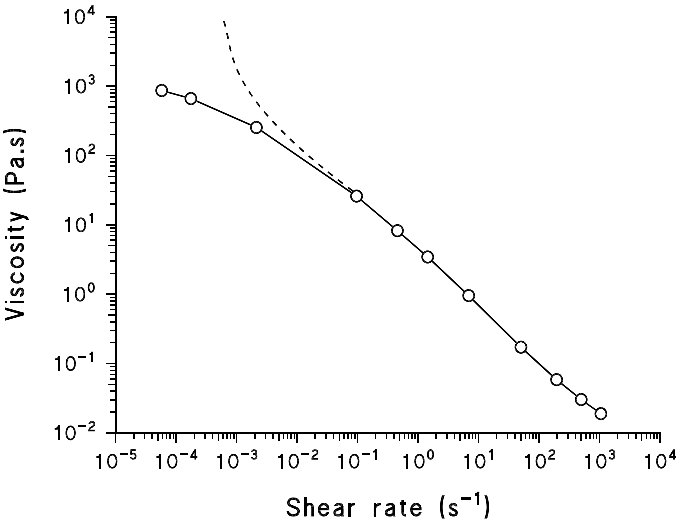

Fig. 2 Same data as figure 1, but viscosity as a function of shear rate on logarithmic axes. Dashed line shows hypothetical behaviour of a solution with a true yield stress.

This study of the effect of xanthan concentration on creaming kinetics was carried it out in order to establish an improved model for the role that xanthan plays in stabilising pourable salad dressings.

The measurement of the velocity of ultrasound across a sample of creaming emulsion can be used to determine the concentration of oil as a function of height [5]. The group at IFR, Norwich has used this technique extensively to characterise creaming emulsions, including their particle-size distribution, creaming kinetics and the nature and degree of their flocculation [6-9].

The creaming behaviour of emulsions can be divided into two types, depending on whether they are flocculated or unflocculated [10].

1) The behaviour of unflocculated emulsions is closer to the traditional picture of dressing stabilisation by xanthan; the emulsion droplets act individually, the large droplets rising faster than the small ones [9]. Therefore, there is no clear interface between the creaming emulsion and the particle-free serum. (Note that the lack of a sharp interface depends on the fact that the emulsion is polydisperse. The creaming or sedimentation of unflocculated, monodisperse colloids gives a sharp interface between the serum and dispersion [10], if the particles are not too small). For unflocculated emulsions, the creaming velocity is governed by some effective viscosity, which depends on the zero-shear viscosity of the serum [11], but also on the emulsion concentration, due to the mutual hindering of the particles [10]. In this case, a suitably modified version of Stokes' law applies.

2) If the emulsion is completely flocculated, the larger droplets do not cream faster than the small ones, since they are stuck together to form a particle network [3]. In this case, creaming is like the collapse (upwards!) of a very weak solid. There is a sharp interface between the particles and the particle-free serum below, consequently visual observation is often sufficient to follow the evolution of the emulsion/serum interface. Robins [9] has suggested that the creaming of completely flocculated, polymer-thickened emulsions is analogous to the flow of polymer solution through a porous medium, the latter being created by the flocculated droplets.

The ultrasound velocity technique is particularly well adapted to distinguishing which of these mechanisms control the creaming of polymer-thickened emulsions [7], and also for determining the mechanism of flocculation [9]. In the past, much has been made of the question of whether the mechanism of polymer flocculation in a particular case is bridging or depletion. For recent discussion of these mechanisms see, for instance, refs. [12] and [13], respectively. In our opinion, it is straightforward to decide which mechanism is operating:

First, the dependence of the degree of flocculation on polymer concentration is completely different. Bridging flocculation has an optimum concentration, at a point where roughly half of the particle surface is covered with polymer. Under these circumstances the probability of collisions between bare surface and polymer-covered surface, which lead to bridge formation, is maximal. At higher polymer concentrations, there are fewer and fewer bare patches, so that the probability of bridge formation diminishes. On the other hand, depletion occurs above some critical polymer concentration, and is complete over a very broad range of polymer concentrations.

Second, the floc-size distribution is different in the two cases [9]. For the concentrated dispersions considered here (volume fraction >10%), bridging flocculation causes all the single particles to be incorporated into small flocs, whereas for depletion flocculated emulsions there is a range of low polymer concentrations where single particles co-exist together with large flocs [7]. In this latter case, a fraction of the droplets move independently, whilst the rest are flocculated and move collectively. This difference is easy to detect using the ultrasound velocity technique [9].

From a physico-chemical point of view, a full-fat pourable salad dressing contains about 40% volume fraction vegetable oil, with a number average droplet diameter of at least 10µm. The aqueous phase contains about 5g/L xanthan and is at least 0.1M in NaCl and typically 0.3M in acetic acid. In this paper we describe the effect of xanthan concentration on the creaming of model salad dressings based on this recipe. The range of xanthan and oil phase concentrations in the model dressings studied here is wider than in previous work [8,14,15], also samples were observed for longer, up to several months. In addition, we concentrate on the early stages of creaming, since from the point of view of a food technologist, the main point of studying creaming is to understand how to avoid it.

Materials and methods

The xanthan was a cell-free sample of CX12 grade, produced by S.B.I., France. Its rheology is similar to that of the CX91 grade, usually used for the preparation of salad dressing. Its characteristics were measured by gel permeation chromatography coupled to a refractive index detector and a Wyatt “Dawn” multi-angle light scatttering detector. Solution rheology was measured using a Contraves LS 30 viscometer for intrinsic viscosity measurements and a

Carrimed CSL 100 rheometer for measurements of the xanthan solution at 5g/L. The flow curve in figures 1 and 2 was measured using creep measurements for shear rates below 1s^{-1}. Special care was taken to ensure that the steady shear rate, long time behaviour was attained at the lowest applied shear stresses.

The xanthan's characteristics were as follows: intrinsic viscosity (in the aqueous phase described below) = 7,100 g/mL; mass-average molecular weight = 5.3 MD; z-average radius of gyration = 180nm. The oil phase was in most cases a mixture of 90% (v/v) heptane and 10% (v/v) hexadecane, as used in previous studies [7,8]. This mixture has the advantages of having a high density difference with the aqueous phase and not suffering from Ostwald ripening (17). Model dressings were formulated using this oil phase with volume fractions of 36%, 18% and 9%. The applicability of the conclusions drawn using alkane emulsions were checked using sunflower oil emulsions. Brij 35 was used as emulsifier for the alkane mixture and either Tween 60 or propylene glycol alginate, PGA (Kelco Kelcolloid LVF), for the sunflower oil. The latter is commonly used as a polymeric emulsifier for salad dressings.

Standard 60% volume fraction emulsions were made in large batches using a Waring blender. Model salad dressings were prepared by mixing concentrated emulsion with xanthan solutions. This method ensured that the emulsion phase was identical between experiments, whereas the usual commercial practice of mixing all the ingredients and then emulsifying allows the presence of different concentrations of xanthan to influence the emulsion size distribution and hence the creaming behaviour. The aqueous phase usually contained 1M NaCl and always 0.3g/L potassium sorbate as a preservative and 0.3M acetic acid. Certain samples were also prepared without NaCl, this did not significantly alter the xanthan solution rheology, since the acetic acid and potassium sorbate provided enough ionic strength to ensure that the addition of the NaCl hardly had any effect (18). The main effect of NaCl addition was to increase the density of the aqueous phase from 1.00g/mL to 1.09g/mL, which increased the buoyancy of the emulsion droplets and thus accelerated the creaming kinetics.

The particle size distribution was measured using the small angle laser light scattering (SALLS) technique (Malvern MasterSizer). The volume average mean droplet diameters were close to 1µm for the alkane emulsion and either 2µm (emulsifier Tween 60) or 6µm (emulsifier PGA) for the sunflower oil emulsions. All the emulsions were highly polydisperse with droplets diameters between 0.1 and 10µm, or even 20µm for the PGA/sunflower oil combination. The size distribution of the emulsions did not vary during the study, so inadequate colloidal stability can be eliminated as an explanation for our results. Creaming behaviour was measured at 20°C using either the ultrasound velocity technique, as described previously [5], or visually. Good agreement was found between the two techniques.

Results

Firstly, the creaming of the alkane emulsion was studied without xanthan addition. As was found previously [6], the particles moved independently and the size distribution calculated using Stokes' law was similar to that obtained by SALLS. However, at xanthan concentrations as low as 0.01g/L this was no longer the case, and a fraction of the droplets creamed much faster than in the absence of xanthan, showing that the emulsion was partially flocculated. For instance, for the 36% volume fraction emulsion at a xanthan concentration of 0.05g/L xanthan, about 6% of the oil phase creamed as separate droplets and the vast majority creamed collectively as a flocculated phase. With xanthan concentrations between 0.1g/L and 5g/L, the highest concentration used, the emulsions were completely flocculated at all oil phase volume fractions. From the arguments given in the introduction, it is certain that the flocculation was due to depletion. This conclusion is in agreement with those of previous studies of xanthan-thickened emulsions [8,14,16].

Perhaps the most interesting observation in this study is that creaming of the flocculated emulsions always occurred in three phases, which are described below. Figure 3 shows some typical data. It shows the height of the sharp boundary between flocculated emulsion and clear serum as a function of time for 36% alkane emulsions containing 0.5, 1 and 2g/L of xanthan. With 0.5g/L of xanthan, the interface started to rise immediately, and more or less linearly, until a concentrated cream formed, whereas for 1 and 2g/L of xanthan, there was an initial delay before creaming started, which was then followed by a sharp transition to linear creaming. This phase continued until all the emulsion had accumulated at the top of the cylinder, after which the concentrated cream continued to compress slowly. These three phases: delay, linear creaming and cream compression, were observed for all the samples above a certain xanthan concentration.

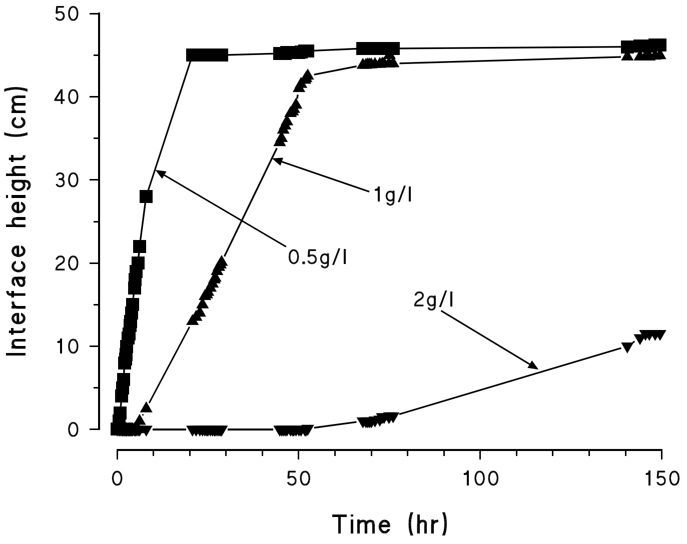

Fig. 3 Evolution of the serum height of a 36% alkane emulsion with 0.5, 1 and 2g/L xanthan in the aqueous phase. Total sample height = 14cm. Lines are to guide the eye.

Their characteristics can be summarised as follows:

1) Initially there is a delay phase during which no creaming occurs and the sample remains perfectly homogeneous, as measured by ultrasound velocity and the naked eye.

2) Creaming begins at a uniform rate with the initial emulsion concentration throughout, apart from a concentrated cream which starts to form at the top of the sample. It is interesting that the transition from the delay phase to creaming is sharp and also that the rate of creaming is close to constant.

3) Uniform creaming finishes when the rising interface between the serum and the flocculated emulsion meets the descending interface marking the boundary between the collapsing flocculated emulsion and the concentrated cream. After all of the emulsion has reached the concentrated cream, it continues to compress slowly due to buoyancy forces. In fact, this final stage overlaps with the second, as the concentrated cream starts to show internal structure quite early in the process of its formation. Several interesting

phenomena occur during the linear creaming and cream compression phases, however a salad dressing which has started to cream significantly is completely unsaleable and so they are not discussed further here.

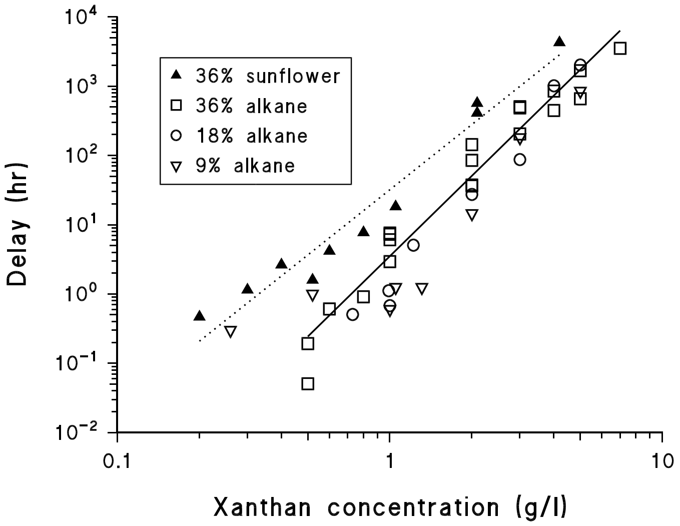

Fig. 4 Length of delay phase as a function of xanthan concentration. Lines are best fits to a power law, dotted line for 36% sunflower oil and solid line for 36% alkane. The slopes are 3.1 ±0.2 and 3.9 ±0.2 respectively.

We now examine the delay phase of creaming in more detail. Figure 4 shows the length of the delay before creaming began as a function of xanthan concentration. The delay varies over more than four orders of magnitude from a few minutes to several months. The delay is clearly longer for the sunflower oil emulsion than for those made with alkane. However, there is apparently no effect of the oil phase volume fraction for the alkane mixture. It can be seen that the delay as a function of xanthan concentration is linear on a log-log plot, i.e. they are related by a power law. However, we do not attach any importance to the slopes, since the points for each oil phase did not all have the same density difference, depending on whether NaCl was present or not. To correct for the variation in density difference, we make the assumption that the delay is inversely proportional to the density difference between oil and aqueous phases, as it is this difference which drives the creaming, whether the emulsion is flocculated or not.

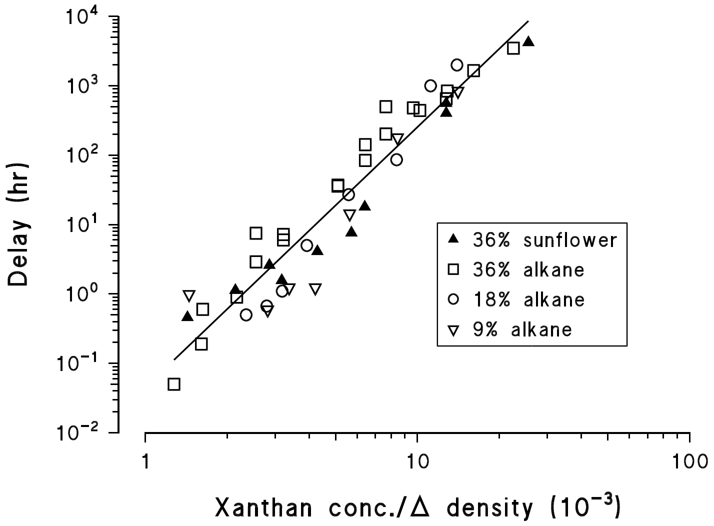

Fig. 5 Length of delay phase as a function of xanthan concentration/(oil/aqueous phase density difference). Line is the best-fit to a power law, slope = 3.6 ± 0.2.

Figure 5 shows the same data as figure 4, but the abscissa is now the xanthan concentration divided by the oil/aqueous phase density difference. This correction collapses the data onto a single straight line, justifying our assumption. The best-fit slope to a power law is 3.6 ± 0.2.

Logically, explanations for the prevention of creaming by xanthan which depend on its solution rheology [14,16] would predict no dependence on the oil phase volume fraction, although the point has not been discussed explicitly, to our knowledge. However, we observed a significant effect of the oil phase concentration for the sunflower oil emulsions prepared with PGA, although not for the alkane emulsions.

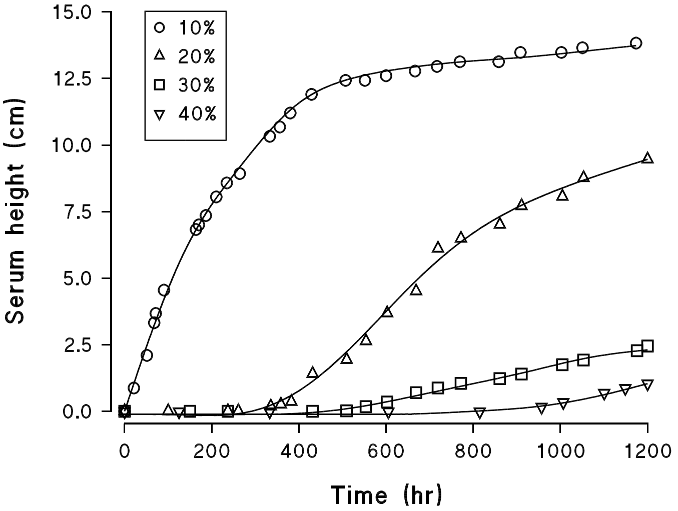

Fig. 6 Effect of the oil phase volume fraction on the evolution of the serum height of a PGA/sunflower oil emulsion with 1.5g/L xanthan in the aqueous phase. Total sample height = 17cm. Lines are to guide the eye.

Figure 6 is similar to figure 3, but illustrates the effect of the oil phase volume fraction on the evolution of the serum height. The data are from visual observation of PGA/sunflower emulsions with oil phase volume fractions between 10% and 40% and a xanthan concentration of 1.5g/L. It shows that with 10% oil there was no delay phase, but at 20% it was already almost 300 hr, increasing to 450hr and 600hr at 30% and 40% oil, respectively. We do not understand why this effect was not observed for the alkane emulsions, but we suspect that it was at least partly due to the difference in their droplet sizes. The volume-average mean size for the alkane emulsions was 1µm and that for the PGA / sunflower samples was 6µm.

Discussion

As discussed in the introduction, the usual model for the stabilisation of emulsions by xanthan addition is the immobilisation of unflocculated droplets by the aqueous phase's yield stress. We have shown that this model is incorrect, as xanthan solutions do not have a yield stress, at least at the concentrations used in the food industry. Nevertheless, everyday experience shows that commercial salad dressings do not cream over periods of up to a year.

Logically, if there really is no creaming at all during this phase, and all the evidence that we have points in that direction, the *dressing* must initially have a yield stress, which decreases with time until it is too small to prevent buoyancy forces taking over, at which point creaming starts. Since the particles are only weakly flocculated, they will retain a certain freedom of movement, so it seems quite reasonable to suppose that the rather open structure formed initially will slowly relax to a more compact one. Unfortunately, it is extremely difficult to check this idea by measuring the very small yield stresses necessary to prevent creaming [3]. Creep measurements must be done using very low applied stresses and waiting for a sufficiently long time, to be sure that the true Newtonian viscosity is obtained. Tests on model dressings showed that creep measurements lasting several hours were too short to measure their Newtonian viscosity. If the measurement is insufficiently long, the Newtonian viscosity is underestimated, so that it is easy to conclude that the flow curve is tending towards a plateau at low applied stresses, when in fact the problem is that measurement times are too short.

Delayed creaming has never been discussed previously, to our knowledge, although a study of the creaming of polymer-thickened emulsions by Dickinson and co-workers shows the existence of a delay phase in certain samples (figures 2 and 3 in ref. [17]). However, Buscall [10] describes two examples of delayed sedimentation in weakly flocculated polymer latex. In one case, weak flocculation was induced by polymer bridging, and in the other the colloid was weakly flocculated by adding sufficient electrolyte to supress electrostatic repulsion and just sufficient non-ionic surfactant to prevent coagulation by van de Waals' attraction. The mechanisms of weak flocculation were thus completely different from depletion by non-adsorbed polymer. On the basis of this evidence, it seems that delayed creaming may be widespread for weakly flocculated dispersions in general, rather than being specific to those which are depletion-flocculated by polymer.

The fact that delayed creaming of dispersions can occur in the absence of polymer suggests a thought-provoking depletion model for dressing stabilisation in which the rheological properties of xanthan are irrelevant, although of course they become important once creaming begins. In this model, xanthan is used because it induces the depletion flocculation of emulsions very efficiently. It does so because it is a very stiff, highly water-soluble, high molecular weight polymer. Of course, these characteristics of xanthan are exactly those which determine its rheology [18-21], but in the depletion model, we regard this as a coincidence. The model proposes that prevention of emulsion creaming is entirely due to the depletion-induced particle network, which has a sufficiently high yield stress to prevent creaming over the shelflife of the product. Van Vliet and Walstra discuss how strong a particle network has to be to prevent sedimentation or creaming [3].

Clearly, on the basis of the data presented here, this depletion model remains speculative. However, the suggestion that the rheology of xanthan has no influence on the prevention of creaming can be straightforwardly tested by comparing the behaviour of a dispersion weakly flocculated by xanthan with that of the same dispersion weakly flocculated to the same extent without xanthan.

For the depletion mechanism to work, we postulate that three conditions must be fulfilled:

Firstly, the polymer concentration must be high enough, because it controls the strength of the interaction between particles [22,23]. Since it is not sufficient for the particles to be just barely flocculated, more polymer than the minimum to cause phase separation will be required. The strength of droplet interaction, and hence the polymer concentration, necessary to prevent creaming in any particular case will depend on the oil/aqueous phase density difference, for obvious reasons, but also on the emulsion concentration and the droplet size, for reasons described in the following paragraphs.

Secondly, the emulsion concentration must be high enough, because it controls the structure of the particle network. In the presence of sufficient polymer to ensure that the interparticle attraction is strong enough, the adhesive particles must then form a network with a yield stress high enough to overcome buoyancy forces. Particle networks can form at extremely low volume fractions, if left undisturbed. Bibette et al. [24] have shown that adhesive emulsions can form space-filling networks at volume fractions as low as 0.01%. Therefore, in practice there is no emulsion concentration below which a continuous network cannot form, assuming that the xanthan concentration is high enough. However, if the emulsion concentration is too low, the network will be too weak to resist buoyancy forces and it will break up into discrete flocs, which cream more rapidly than the individual particles. In this situation, creaming can be slowed, but never delayed, by using high xanthan concentrations. This is what Luyten et al [16] observed in their study, where the emulsion volume fraction was only 4%: depletion flocculation always accelerated creaming, and no delay phase was observed.

Thirdly, the ratio of the particle radius to the polymer radius of gyration, R_g, must be greater than 4 , because this controls the nature of the particle flocs. This condition is due to the phase behaviour of colloid/polymer mixtures. Theory predicts [25-27] that if the particle radius is less than about three times the polymer R_g, the flocculated particle phase will be liquid, not solid. Under these circumstances, a particle network cannot form. Leal-Calderon has confirmed this prediction experimentally [28]. He observed polymer latex/hydroxy ethyl cellulose mixtures with phase-contrast optical microscopy. When the particle radius/R_g, was 3.5, the latex formed a separate phase of large drops (diameter ≈30μm) with fluctuating interfaces, containing freely moving particles. When the ratio was 4.2, the flocs were rigid, and the constituent particles were only free to oscillate around a fixed position inside them.

We think that the need to fulfill this third condition may at least partly explain the differences between our results and those of Dickinson et al's very recent study (16). They studied the creaming of an 18% volume fraction alkane emulsion as a function of added xanthan concentration, so results similar to ours might be expected. However, this is not at all the case, firstly, they never observed delayed creaming, even at xanthan concentrations as high as 6g/L. At this concentration, we found a delay time of several months for an 18% alkane emulsion. They also observed several phenomena which we never encountered: for instance, the appearance of a sharp increase in emulsion concentration near the bottom of the sample, which did not rise for several days. Especially notable is the appearance in a few hours of a continuous emulsion concentration gradient throughout the sample, with no serum layer at the bottom, or cream layer at the top. This behaviour cannot be fitted into our depletion model, and indeed it has not been observed in any of the Norwich group's previous studies of emulsion creaming [5-9]. We have no precise explanation for these very significant differences, but a possibility is that their system did not fulfill our third condition: the volume-surface average diameter of their emulsion droplets was 0.65μm and the xanthan that they used we know to have similar characteristics to ours, i.e. a radius of gyration of about 0.2μm. On this basis, their particle diameter/R_g ratio was about 3 (the polydispersity of both emulsion and xanthan prevent the calculation of a precise figure) so, according to Leal-Calderon's results [28], it is possible that their flocculated phase was liquid and not solid. Observing the appearance of their samples using phase-contrast optical microscopy provides a simple method of checking this suggestion.

The effect of droplet particle size on the prevention of emulsion creaming has not been discussed previously. In the traditional explanation, its role is obvious, because a modified Stokes' law is assumed to apply and so larger particles have higher buoyancy and require a higher aqueous phase yield stress to prevent their creaming. However, once it is admitted that the emulsion is depletion flocculated, so that the droplets cream collectively, either in flocs or all together, the effect of particle size is not clear. Assuming that condition 3) has been fulfilled two competing effects can be imagined:

i) All other things being equal, the pair interaction due to depletion between large droplets is larger than that between small ones (they are "stickier") (24,25). For instance, Luyten et al. (15) calculated a well depth due to depletion of ≈3kT for a 0.2μm droplet and 9kT for a 0.8μm droplet (at a separation of 10nm. and a xanthan concentration of 0.2g/L). Another example is the use of the particle size dependence of depletion flocculation to fractionate dilute emulsions (31). Bibette used surfactant micelles instead of polymer to induce depletion flocculation. With increasing micelle concentration, the large droplets flocculate first and cream rapidly, whilst the smaller droplets remain unflocculated. Each increase in micelle concentration flocculates a smaller size of particle. If this were the only effect of particle size, the depletion model predicts that increasing the particle size will make stabilisation easier. This prediction is counter-intuitive in the context of the traditional model for stabilisation, and if verified is good evidence that the depletion model is correct. However, another effect can be imagined which goes in the opposite direction:

ii) Increasing the particle size, at constant oil volume fraction, will decrease the number of contacts between particles, because there are fewer of them and hence weakening the particle network.

Thus when the particle size increases, the bond strength in the particle network increases, due to i), but the number of bonds goes down, due to ii). Hence, the net effect of increasing particle size is not straightforward to predict.

Conclusions

Rheological measurements of an aqueous phase typical of a pourable salad dressing showed that there was no yield stress. Also, it has been shown that xanthan completely flocculates the droplets of model pourable salad dressings by a depletion mechanism, at concentrations much lower than those used commercially. Therefore it is concluded that the addition of xanthan prevents creaming by flocculating the emulsion to create a weak gel-like structure, rather than by conferring its solution rheology on the dressing, which is the usual explanation. Dressing stabilisation is due to the repulsive interaction between emulsion droplets and xanthan molecules. This interaction creates a time-dependent yield stress, which is initially large enough to prevent creaming.

The depletion model has a number of advantages over models which explain stabilisation by xanthan rheology, in particular it incorporates the effects of both oil phase concentration and droplet size, which are not adressed by other models. It also provides a plausible explanation for delayed creaming.

In salad dressings, and in all the other foods suffering from similar problems which come to mind, what is required is not slow creaming, but no visible creaming over the product's shelflife. Therefore the discovery that creaming is delayed, although not indefinitely, is important for the formulation of acceptable products. If our results are as general as we suspect them to be, correct formulation to prevent creaming can be summed up as: *adding just enough xanthan to make the delay phase exceed the shelflife*. Of course, this is a very one-dimensional view of the formulation process, where many different textural, economic and processing constraints must be satisfied simultaneously. Nevertheless, shelflife testing to check that a dressing does not suffer from creaming is an important part of the formulation process (such testing also checks for problems of coalescence, a problem which we have not addressed here).

Measurements of the creaming of model dressings show the presence of an initial delay phase, during which the sample does not change macroscopically and no creaming occurs.

Subsequently, linear creaming begins. The length of the delay phase shows simple scaling with the xanthan concentration and the oil/aqueous phase density difference. These results form the basis of a new model for the stabilisation of salad dressings by xanthan. It could be used to help define improved accelerated shelflife tests and to understand better the relationship between dressing rheology and xanthan concentration.

Acknowledgements

We thank Rachel Dann for carrying out some creaming experiments. A.P. thanks Jerôme Bibette, Gerard Cuvelier and Bernard Launay for useful discussions, as well as Jim Jindra and Jim Carr of S.B.I. Inc. for explaining the formulation of salad dressings.

References

1. D. C. H. Cheng, Rheol. Acta **25,** 542 (1986).
2. H. A. Barnes and K. Walters, Rheol. Acta **24,** 323 (1985).
3. T. van Vliet and P. Walstra in *Royal Society of Chemistry Special Publication 75: Food Colloids*, Royal Society of Chemistry 206 (1989).
4. A. Giboreau, G. Cuvelier, and B. Launay, J. Texture Studies **25,** 119 (1994).
5. A. M. Howe, A. R. Mackie, and M. M. Robins, J. Dispersion Sci. Technol. **7,** 231 (1986).
6. C. Carter *et al.*, Prog. Colloid Polym. Sci. **76,** 37 (1988).
7. A. J. Fillery-Travis, P. A. Gunning, D. J. Hibberd, and M. M. Robins, J. Coll. Inter. Sci. **159,** 189 (1993).
8. P. A. Gunning, D. J. Hibberd, A. M. Howe, and M. M. Robins, Food Hydrocolloids **2,** 119 (1988).
9. M. M. Robins, ACS Symp. Ser. 448, 230 (1991).
10. R. Buscall, Colloids and Surfaces **43,** 33 (1990).
11. R. Buscall, J. W. Goodwin, R. H. Ottewill, and T. F. Tadros, Journal of Colloid and Interface Science **85,** 78 (1982).
12. E. G. M. Pelssers, M. A. Cohen Stuart, and G. J. Fleer, J. Chem. Soc. , Faraday Trans. **86,** 1355 (1990).
13. P. D. Patel and W. B. Russel, J. Colloid Interface Sci. **131,** 201 (1989).
14. E. Dickinson, J. Ma, and M. J. W. Povey, Food Hydrocolloids **8,** 481 (1994).
15. H. Luyten, T. van Vliet, and W. Kloek, 527.
16. H. Luyten, M. Jonkman, W. Kloek, and T. van Vliet in *Royal Society of Chemistry Special Publication 113: Food Colloids and Polymers: Stability and Mechanical Properties*, Royal Society of Chemistry 224 (1993).
17. Y. Cao, E. Dickinson, and D. J. Wedlock, Food Hydrocolloids **4,** 185 (1990).
18. C. J. Carriere, E. J. Amis, J. L. Schrag, and J. D. Ferry, J. Rheol. **37,** 469 (1993).
19. G. Cuvelier and B. Launay, Carbohydr. Polym. **6,** 321 (1986).
20. M. Milas, M. Rinaudo, M. Knipper, and J. L. Schuppiser, Macromolecules **23,** 2506 (1990).
21. Y. Takada, T. Sato, and A. Teramoto, Macromolecules **24,** 6215 (1991).

22. S. Asakura and F. Osawa, J. Chem. Phys. **22,** 1255 (1954).
23. A. Vrij, Pure Appl. Chem. **48,** 471 (1976).
24. J. Bibette, D. Roux, and B. Pouligny, J. Physique. II **2,** 401 (1992).
25. A. P. Gast, C. K. Hall, and W. B. Russel, J. Colloid Interface Sci. **96,** 251 (1983).
26. H. N. W. Lekkerkerker *et al.*, Europhys. Lett. **20,** 559 (1992).
27. B. Vincent, J. Edwards, S. Emmett, and R. Croot, Colloids Surf. **31,** 267 (1988).
28. F. Leal-Calderon, PhD, University of Bordeaux (1992).

Chapter 3

Delayed sedimentation as a paradigm for formulating gravitationally stable dispersions

There are no scientifically well-founded tests to predict the shelf life of colloidal dispersions. Here “shelf life” means “time without visible effects of gravitational instability”. Prediction is difficult because visible sedimentation is often neither immediate nor absent. Instead, it starts suddenly after a delay that may be several months. Delayed sedimentation occurs in a wide range of weakly flocculated colloidal dispersions. These systems are temporarily trapped (jammed) far from equilibrium. When jamming is too weak the system sediments immediately. When jamming is too strong, then the system “never” sediments. Jamming is favoured by: high volume fraction, strong flocculation and low gravitational stress. The phenomenology of delayed sedimentation is reviewed, concentrating on emulsions depletion-flocculated by polymer. New data are presented for scaling of the delay time with polymer volume fraction and gravitational stress. They provide practical aid for formulation and insight into the form of a theory. There is no theory yet to predict the delay time. Possible elements of a theory are discussed.

To be submitted to
Advances in Colloid and Interface Science

Introduction

The sedimentation and creaming[1] of concentrated colloidal dispersions is a problem in a broad range of industries (food, crop protection, home care, cosmetics, pharmaceutical, etc.). Adding polymer is the usual method to produce gravitationally stable formulations. It is important to add the right amount of polymer, as adding too much will degrade key properties of the product, such as its pumpability or pourability. There is now broad agreement that the polymer's main effect is to induce formation of a depletion-flocculated particle gel. However, the exact mechanism by which gravitational instability is prevented remains controversial. This lack of understanding is a severe technological handicap, as without it we have no scientifically based test to predict how gravitation limits a product's shelf life. I argue that the problem can be understood in the framework of delayed sedimentation [1]. This article summarises progress towards answering two questions: 1) "What test could predict the shelf life of an arbitrary weakly flocculated colloidal dispersion?" 2) "What information is needed to predict the shelf life directly from the sample's characteristics?" The article has a technological perspective, while incorporating ideas from fundamental studies.

Sedimentation has been studied by separate communities of formulation scientists, colloid scientists, chemical engineers [2] and soft-matter physicists; sometimes they have made the same discoveries independently. Each community concentrates on different aspects. The distinctive point of view of formulation scientists, taken here, is that their aim is to avoid visible sedimentation. They want to predict for how long a sample will be stable. The rate of sedimentation, once its effects are visible, is of no direct interest. More than ten years ago Parker et al. [1] showed that many flocculated emulsions are stable by eye for a well-defined time: these samples show delayed sedimentation. They suggested that delayed sedimentation could be used as a paradigm for formulating gravitationally stable dispersions, summarized by the aphorism: "Make the delay time longer than the shelf life". Since then, significant progress has been made in understanding the phenomenon, but from a formulator's point of view the central issues remain unanswered.

The samples concerned are all completely flocculated colloidal gels, so when sedimentation occurs, the serum is almost completely transparent. The particle concentration is high enough that gelation is much faster than sedimentation. Therefore the samples all gel completely and rapidly, so neither the extent of flocculation nor competition between gelation and sedimentation [3] are relevant.

Sedimentation of a colloidal gel is driven by the gravitational stress. The maximum gravitational stress is given by: $\tau_g = \Delta\rho g \phi h$, where τ_g is the gravitational stress, $\Delta\rho$ is the density difference between particles and serum, ϕ is the particle volume fraction and h is the sample height.

---

[1] Although creaming is often discussed as a separate phenomenon, there is no difference between the phenomenology and theory of sedimentation and those of creaming, so the term "sedimentation" will be used here to encompass both.

The criterion for a visually stable sample is that the rate of fall or rise of the dispersion/serum interface is just small enough that no visible particle-free liquid appears over the shelf life of the sample:

$$v < v_{sl} = h_{crit}/t_{sl}$$

v is the average interfacial velocity. v_{sl} is a critical value of the interfacial velocity; smaller velocities give visually acceptable samples. h_{crit} is the critical height of the interface at which the sample's appearance becomes unacceptable and t_{sl} is the shelf life. In an inelastic colloidal gel, the interfacial velocity is given by Darcy's law:

$$v = -\frac{k}{\eta}\nabla p$$

with ∇p the pressure gradient, k the network permeability and η the viscosity of the continuous phase. In a finite sample, this expression has to be corrected for the backflow of solvent [4] and for finite sample width.

Buscall's 1990 review [4] is still a good overview of sedimentation, although it is inevitably becoming dated. He was the first to report delayed sedimentation: the sample appears stable for a certain time and then suddenly starts to sediment. However, he gave the phenomenon no special significance. He also noted that small changes in conditions cause delayed sedimentation to change to immediate, slow ("creeping") sedimentation. This sensitivity to initial conditions, such as the shape of the container [5], makes the definition of a comprehensive theory very challenging.

Auzerais et al's articles [6,7] provide a solid framework for understanding the sedimentation of dispersions. They formulate and solve the equations of motion of a settling dispersion as a set of 1D partial differential equations. The relevant dimensionless groups are explained. They find solutions that are well verified experimentally for both hard spheres and strongly flocculated systems. However, the model breaks down when the flocculation is weak, because their constitutive equations are not time-dependent. This is exactly the area that interests us here. Further, since their formulation of the problem is 1D, the authors explicitly state: "Effects such as … channelling are not considered" [6]. See below and reference [8] for a discussion of channeling. The use of a 1D model also means that wall effects cannot be included.

Buscall and White [9] established the three key factors controlling the settling of weakly flocculated dispersions: the dispersion's gel point, sediment compressibility and sediment permeability. In a 1D colloidal gel, two main forces prevent sedimentation: porous media flow and elasticity. In principle, either or both may provide significant contributions. For a thin horizontal slice, the 1D poroelastic equation equates the gravitational stress (G) with the sum of the pressure due to fluid flow (P) and the sample's compressive elasticity (E): G = P + E or P = G – E:

$\Delta\rho g\phi(z) = \frac{\eta}{k}v + \frac{\partial\sigma}{\partial z}$. Where z is the distance from the bottom of the container, $\phi(z)$ is the particle volume fraction as a function of height and $\partial\sigma/\partial z$ is the vertical stress gradient. Rearranging for the settling velocity: $v = \frac{k}{\eta}\left(\Delta\rho g\phi(z) - \frac{\partial\sigma}{\partial z}\right)$.

This equation shows that the gravitational stability is not generally due to *either* elasticity *or* flow through a porous medium. A particular sedimentation rate can be due entirely to Darcy flow, entirely to elasticity or to any proportion in between.

The next section summarizes the phenomenology of delayed sedimentation. Then the possible elements of a theory of delayed sedimentation are discussed. Finally, a possible rheological correlate with delayed sedimentation is discussed, before concluding.

Phenomenology of delayed sedimentation

Delay - The essential phenomenon

The archetypal phenomenon is very easy to observe. Figure 1 shows some typical data for a vegetable oil-in-water emulsion thickened with xanthan, a stiff, high molecular weight polysaccharide. The volume fraction of emulsion is 0.2. The droplets are polydisperse with diameters between 1 and 10μm. The height of the sharp cream line, tracked by eye, is plotted as a function of time for xanthan concentrations of 0.5, 1 and 2g/kg.

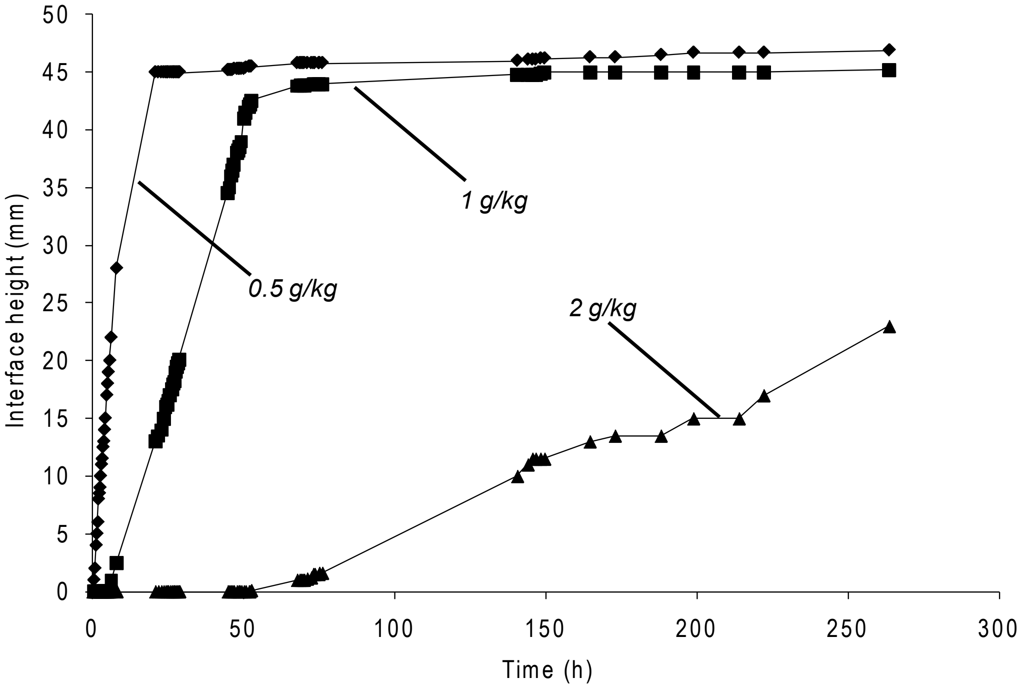

Figure 1 Delayed creaming of 20% oil in water emulsion with 0.5 g/kg (◆), 1g/kg (■) and 2g/kg (▲) of xanthan. Lines are to guide the eye.

With 0.5g/kg of xanthan there is no delay, whereas it is about 8 hours for 1g/kg and 50 hours for 2g/kg. In all cases, the interface is sharp and the colloid-poor phase is transparent, so the system is completely flocculated. What this graph makes clear is that there is a sharp transition from *immediate* creaming (for 0.5g/kg of xanthan) to *delayed* creaming (for 1 and 2g/kg). Note that as the polymer concentration increases, the initial slope does not gradually decrease to a low level, but, over a small concentration range, suddenly snaps from *fast immediate* creaming to no visible creaming for a finite time. It is also interesting that the rates of creaming are very constant within each phase. There is no evidence in these sedimentation profiles of continuous, slow changes in structure. These kinetics contrast with those of creeping sedimentation [4] for which the profile of interface height against time is close to exponential [10,11].

Plots very similar to figure 1 can be found in several papers [12-15]. These studies are all concerned with polymer-thickened emulsions, so the continuous phase is much more viscous than water and the density difference between phases is small, in contrast to the dense inorganic particles used in many studies of sedimentation [3,7,16,17].

Delayed sedimentation cannot be understood by correcting either Stokes' law or Darcy's law. Both would result in *immediate* sedimentation. On the other hand, the presence of a permanent yield stress is not a possible explanation, as this would result in *permanent* stability. The phenomenon is qualitatively different from the results expected for either of these explanations. Since Parker et al [1] first made this point, it has become clear that in many cases imperceptibly slow sedimentation occurs during the "delay". Thus, delayed sedimentation is just a particular case of the much more widely observed slow-fast sedimentation.

Slow-fast sedimentation

In most studies of the sedimentation of flocculated dispersions, the profiles are not like those shown in figure 1. Instead, there is no apparent delay, but rather the initial slow-but-visible sedimentation is followed by a sudden increase in settling rate [3,18,19]. I argue that the difference between these two classes of sedimentation is only apparent.

Tuinier and de Kruif [11] used a high resolution optical scanner [20] to show that for their polymer-thickened emulsions, slow creaming occurs during the delay phase. Using the same equipment, we have found similar results. The graph below shows some typical data.

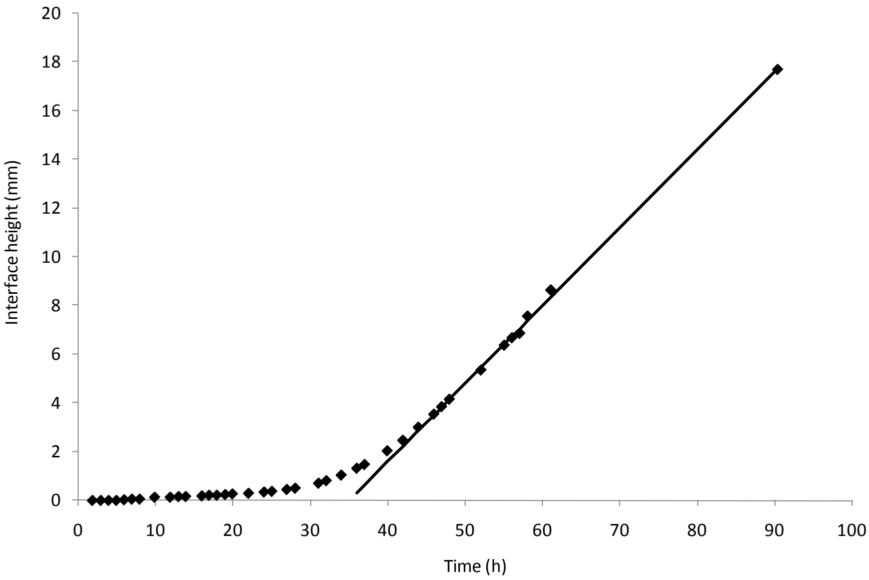

Figure 2 High resolution data for kinetics of delayed sedimentation. Interface height as a function of time was determined from the backscattered light with an optical scanner. 20% emulsion and 1.5g/kg xanthan. Intercept on the time axis gives a suitable definition of the delay time.

This result suggests that slow-fast sedimentation and delayed sedimentation are similar phenomena. The only difference between them is that in delayed sedimentation the initial rate of sedimentation is invisible to the naked eye.

Allain et al. [3] studied the slow-fast sedimentation of dilute, strongly flocculated calcium carbonate. They found that the initial slow rate of sedimentation was well described as Darcy flow through impermeable spheres having the size of aggregates generated by diffusion limited aggregation: $v(\phi) \propto (\phi)^{-1.9}$. What difference in initial sedimentation rate should we expect between their system and a typical well stabilized, polymer-thickened emulsion? Increasing ϕ from 0.1 to 10% volume fraction decreases the settling rate by about 5,000 times. The density difference in their system is 1.7g/mL, whereas for vegetable oil/water it is only about 0.1g/mL: a factor of about 20. The viscosity of their continuous phase is close to 1mPas, whereas in polymer-based systems it is at least 100mPas and often much more. Therefore the Darcy settling rate can easily be 10^6 times slower in a typical polymer-thickened emulsion, compared to the dilute systems of dense particles studied by Allain et al. They find a sedimentation rate of about 10µmh^{-1} at a volume fraction of 0.1%. Therefore, no change in the underlying physics is needed to explain the apparent delay observed in polymer-flocculated, emulsion-based systems and the slow-fast sedimentation seen in dilute systems of dense mineral particles suspended in unthickened solvent.

This calculation shows that, as long as delayed sedimentation does not intervene, it is not difficult to formulate polymer-thickened dispersions as stable products. Hence the proposition of the title: a central issue for the formulator is to understand, predict and avoid delayed sedimentation.

Effect of polymer concentration

If elasticity is negligible, then we expect immediate creaming at a rate set by Darcy's law. In this case, adding polymer simply decreases the rate of creaming in inverse proportion to the zero shear viscosity of the continuous phase. As Kilfoil et al put it: "the viscosity sets the time scale for the process" [19].

If this were the only effect of adding polymer, then we expect the delay time to scale linearly with the viscosity of the continuous phase. It actually scales with viscosity to some power significantly greater than one [12,19]. Therefore, the added polymer must also change the structure of the colloidal gel. Parker et al found that the delay time scaled with the concentration of xanthan as approximately c^4. Poon et al. [15] and Kilfoil et al [19] found that the delay time was proportional to the exponential of the free polymer concentration. Neither of these forms can be universal, since Figure 1 shows that for low enough polymer concentrations, there is zero delay. More data over a broad range of polymer concentrations is required to find a broadly applicable relationship.

Effect of colloid volume fraction

Delay is only observed at intermediate volume fractions. When the volume fraction is too low, sedimentation is immediate. When it is too high, sedimentation "never" occurs. "Never" is defined by the experimentalist's patience. Between these limits, the higher the volume fraction, the longer is the delay. This trend is intuitive, as at high enough volume fraction, even an unflocculated sample will be jammed permanently at time zero.

In the limit of strong flocculation, Allain et al. [3] defined the maximum volume fraction for which gravitational forces prevent gel formation (ϕ^*). They give:

$$\phi^* = \left(\frac{4\pi\Delta\rho g a^4}{3kT}\right)^{(3-D)/(1+D)}$$

With a the particle radius and D the fractal dimension of the flocs. They also found experimentally a concentration ϕ^{**}, close to $\phi = 0.05$ in their system, above which sedimentation never occurred. They argue that it is reasonable to assume that ϕ^{**} is the minimum concentration for the sample to have a compressive yield stress. These two concentrations set limits on the range over which delayed or slow-fast sedimentation can be observed, for strongly flocculated dispersions.

Away from the limit of strong flocculation, Bergström et al. [16,21] determined the compressive yield stress of flocculated dispersions by combining centrifugation and gamma-ray scanning. They determined its variation at equilibrium, for dispersions with energies of interaction between -10 and -50kT at closest approach. They obtained good fits to the empirical function:

$$\sigma = \frac{\sigma_0 \phi^n}{(\phi_{max} - \phi)}$$

With σ_0 proportional to the interaction energy, ϕ_{max} inversely proportional to the interaction energy and the exponent, *n*, a constant, close to 3.2. This function sets a limit on ϕ^{**} for their system.

These studies set limits on the range over which delayed, or slow-fast, sedimentation occur.

Effect of polymer structure and molecular weight

I assert that any polymer can induce delayed sedimentation. Figure 2 validates this assertion by showing new data for the delay time as a function of polymer concentration for six different water-soluble polymers. They were chosen to cover a range of properties: stiff and flexible, high and low molecular weight, branched and linear, polyelectrolyte and neutral.

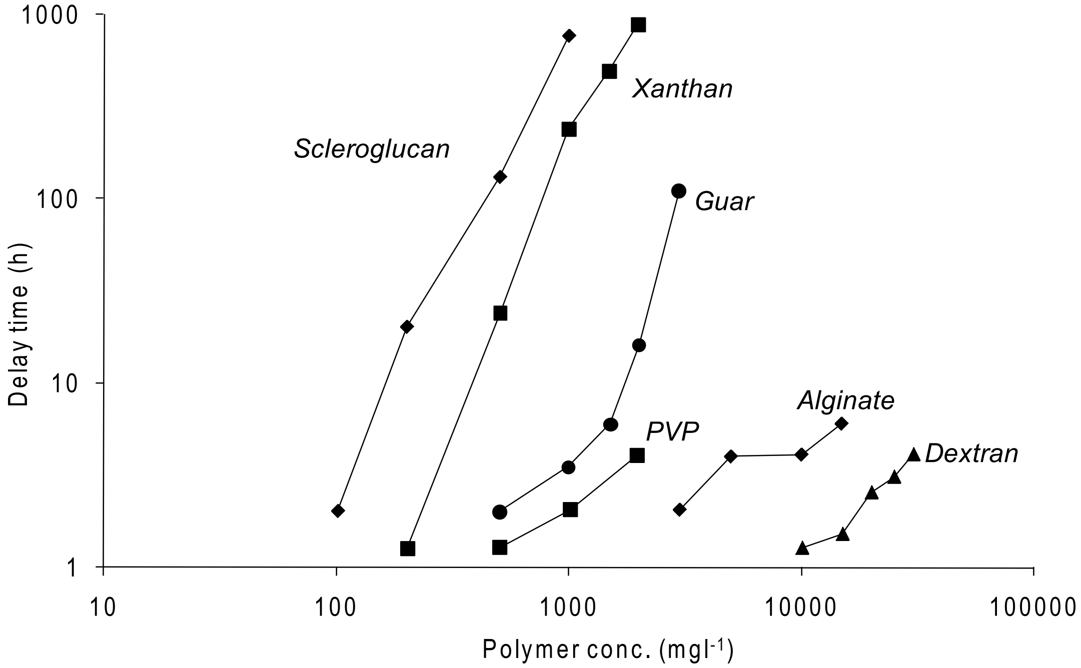

Figure 3 Delay time as a function of polymer concentration for six polymers. Emulsion: volume fraction = 0.4, droplet diameter = 1-10μm. Solvent = 0.1M NaCl. Polymers [intrinsic viscosity in mL/g]: scleroglucan [16,400]; xanthan [9,900]; guar [2,100]; sodium alginate [1,300]; poly vinyl-pyrollidone [170]; dextran [40].

The figure below shows that this data collapses onto a single curve, if the polymer concentration is made dimensionless by scaling with the intrinsic viscosity, $[\eta]$.

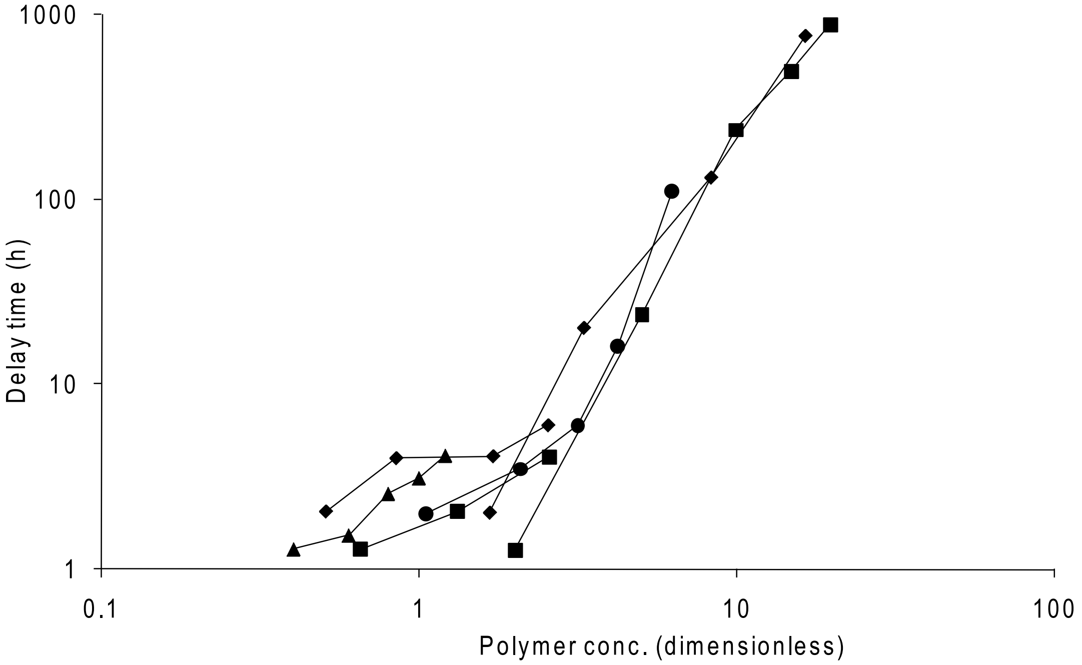

Figure 4 Delay time as a function of dimensionless polymer concentration. Data taken from figure 3.

Here is a simple argument justifying this scaling: The depletion-induced phase behaviour of polymer/particle mixtures depends three factors: the size ratio of polymer to particle, the volume fraction of polymer and the volume fraction of particles [22]. In this case, the volume fraction of particles is constant and the polymer/particle size ratio is small (<0.1), so it is reasonable to assume that the only controlling factor is the polymer volume fraction given by:

$\phi_p = \frac{4}{3}\pi R_g^3 n_p$, with R_g the polymer's radius of gyration and n_p the number concentration of polymer molecules. Now c_p, the polymer concentration in weight per unit volume, is given by:

$c_p = \frac{4n_p M}{N_A}$, with *M* the polymer molecular weight and *N_A* Avagadro's number. The polymer's intrinsic viscosity is related to its radius of gyration by the Flory-Fox equation: $[\eta] = \frac{\Phi'}{M} R_g^3$ where Φ' is a universal constant. Substituting and rearranging, we obtain: $\phi_p = \frac{4}{3}\pi \frac{M[\eta]}{\Phi'} \frac{c_p N_A}{4M} = \frac{1}{3}\pi \frac{N_A}{\Phi'}\left(c_p[\eta]\right)$, so we find that the polymer volume fraction is proportional to the dimensionless polymer concentration. If these results prove to be general, they provide a straightforward method to predict how changing the polymer concentration, structure and molecular weight will affect the delay time.

Reinforcing these results, Velez et al. [12] studied the effect of three polysaccharides on the creaming kinetics of a 10% emulsion. They showed that the delay time scaled with the zero shear viscosity, independent of the polymer used. Their dependence of delay time on viscosity has a similar form to that shown in Figure 3.

Effect of gravitational stress

Sedimentation is driven by the gravitational stress, after corrections for the wall stress. The gravitational stress can be varied over a narrow range by varying the sample height [5,10,23]. To vary the gravitational stress over a wider range, centrifugation must be used. We observed samples while centrifuging successively for many short periods. We used a swing-out rotor, so that the gravitational stress was imposed axially. A series of samples were centrifuged at three different rates. To see whether the end of the delay had occurred, the centrifugation was stopped periodically and the samples examined by eye. The figure below shows the delay time for centrifuged samples as a function of the delay time for the same sample at 1g.

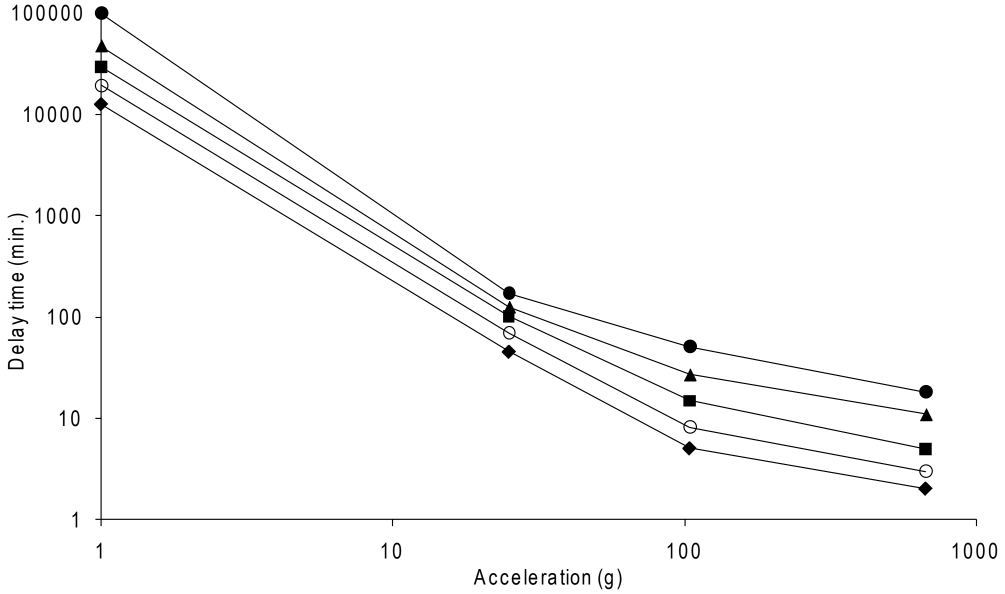

Figure 5 Delay time for five samples during centrifugation and under ambient conditions. Emulsion volume fraction = 0.2; xanthan concentration = 0.2, 0.22, 0.24, 0.27 and 0.3gL^{-1}, going from bottom to top. Lines are to guide the eye.

The data form a set of parallel curves, with the higher polymer concentrations giving longer delay times, as expected. The simple and coherent relation between delay time at different gravitational accelerations has not been previously reported. These data provide proof-of-concept for a rational accelerated shelf life test. However, more data is required to provide solid correlations between results under ambient conditions and under centrifugation.

Senis and Allain [23] made a thorough test of the effect of sample dimensions on the *equilibrium* sediment height for their system of strongly flocculated calcium carbonate over a range of low concentrations ($10^{-4} < \phi < 10^{-1}$). They found a critical height and a critical width. Samples with at least one dimension below the critical values were stable. Their theoretical analysis assumes that two forces oppose gravitational compression: wall friction and a compressive yield stress. The existence of wall friction implies that a narrow enough sample will be stable at all heights, while the existence of a yield stress implies that short enough samples will be stable at all widths. These explanations only apply to systems at equilibrium. We know that some samples showing delayed sedimentation do not have yield stresses, at least at short times, due to Poon et al's observation that their samples could be sheared continuously or disrupted early in life, without affecting the delay time [15].

Bergström studied the effect of sample width on the equilibrium sediment height of weakly flocculated alumina dispersions [21]. He showed the following relation between the equilibrium height for a sample of finite and infinite width: $\frac{1}{h_{eq}(r)} = \frac{1}{h_{eq}(\infty)}\left(1 - \frac{2S_w}{r(d\sigma/dz)_\infty}\right)$ with τ_w the wall stress and r the sample width. Thus a plot of $1/h_{eq}$ against $1/r$ is a straight line whose slope and intercept can be used to determine the wall stress and the equilibrium height in the absence of wall stress, respectively.

Starrs et al. [5] studied the effect of sample width and height on delay time. They found a critical width and a critical height, above which the delay time was independent of width or height. This result is similar to those of both Michaels and Bolger, for the initial sedimentation rate [24], and Senis and Allain, for the equilibrium sediment height [23].

Kim et al. [10] show clearly how delayed sedimentation changes to creeping sedimentation as the sample height is reduced.

Effect of mechanical disruption on delay time

An intuitive idea for the mechanism of delayed sedimentation is that the particle gel is initially strong enough to support its own weight and subsequently weakens, due to coarsening. The end of the delay then corresponds to a percolation threshold when the structure becomes too weak to support its own weight. This idea is shown not be universally applicable by two experiments described by Poon et al. [15]. In the first they simply placed a metal ball in a sample early in the delay and moved it through the gel with a magnet. The damage induced by this movement had no influence on the delay time. To quantify this effect, they also observed delayed sedimentation inside the transparent, concentric cylinder geometry of a stress-controlled rheometer [15]. Low shear stresses had no effect on the delay, whereas higher values shortened the delay. In all cases, the samples were subjected to large strains, without losing the essential features of delayed sedimentation. This key observation separates delayed sedimentation from the breakdown of solids. In delayed sedimentation, the structure can be broken and re-heals, at least in the early stages.

In any case, the idea of a weakening structure as the origin of the delay is countered by rheological measurements, which show that the structure is actually getting stronger [15]. This observation is counterintuitive: it seems unlikely that a structure that is hardening is also getting closer to catastrophic breakdown. The key point is that at the same time the structure is also becoming less reversible and more brittle and so more prone to fracture. The observation of hardening also fits with the relevance of universal ageing shown by Cipelletti et al.'s study [25] of a strongly flocculated colloidal gel, which is discussed below.

Towards a theory of delayed sedimentation

Despite intense study of delayed sedimentation by several groups, nobody has yet proposed a theory to explain or predict the phenomenon. Here, I suggest some directions that look promising.

The jamming paradigm

The jamming paradigm [26] unifies observations and theory concerning a wide range of systems trapped far from equilibrium. Window glass, powder-choked pipes and traffic jams are familiar examples. Trappe et al [27] showed the generality of the jamming paradigm for weakly flocculated colloidal dispersions. The key variables are the same as for delayed sedimentation: strength of flocculation, stress and volume fraction. However, time is absent from their picture. Several authors have shown state diagrams for delayed sedimentation with particle volume fraction and polymer concentration (or polymer volume fraction) as the axes [11,13,15,28]. The figure below shows some typical data.

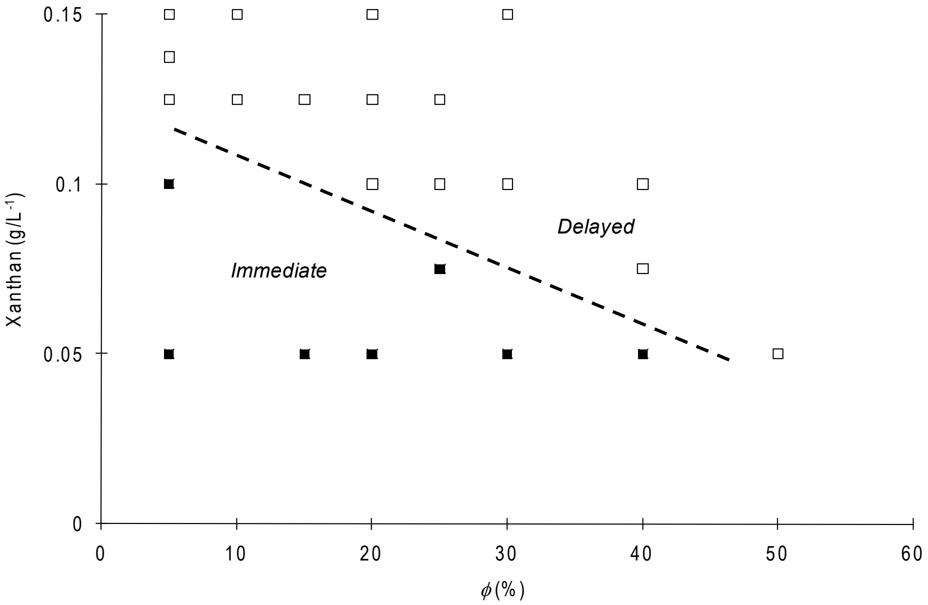

Figure 5 State diagram for delayed sedimentation as a function of polymer concentration and volume fraction. Line is to guide the eye.

There is a typical tradeoff between volume fraction and polymer concentration. A border can be traced where delayed sedimentation starts. In the region where delayed sedimentation occurs, there are isochrones of equal delay time, rather like layers of an onion. However, unlike onion layers, the isochrones converge as the volume fraction increases. This convergence is imposed by the constraint that no polymer is required for permanent stability at particle volume fractions above the jamming limit.

Delayed fracture

Connecting delayed sedimentation to delayed fracture [29] is a novel approach. I justify the connection by the following parallels:

1) Several groups [3,15,28,30] have shown that the appearance of a sample-spanning vertical fracture is the clearest sign of the start of fast sedimentation.

2) The scaling with accumulated gravitational stress, shown in figure 4, demonstrates that the time between successive applications of high stress is irrelevant. This is typical of the delayed fracture of brittle materials [29]. The key idea is the irreversible accumulation of "damage": microcracks that have little effect on the bulk properties until some threshold concentration is reached.

Manley et al [30] used a clever trick to show when fracture occurred in their flocculated dispersions: they filled half of the base of their sample with a block with a square cross section. If the sample is elastic, then a crack will be formed at the corner of the block, due to concentration of stress, and a step appears at the surface of the sample. The step disappears at the start of fast sedimentation, showing that the sample has become fluid at this time.

Delayed (or sub-critical) fracture occurs at stresses below the critical stress, σ_c, which causes immediate fracture. For wood, Guarino et al. showed [29] that the failure time scaled with the applied stress as , with t_f the fracture time, t_0 a prefactor, P_0 the pressure for immediate breaking and P the applied pressure. Further, they showed that the delay could be predicted for an arbitrary history of applied stress by considering that each sub-critical stress causes a given rate of damage.

In brittle solids, damage initially accumulates slowly, until there is a sudden acceleration close to the time when a sample-spanning crack forms. A damage variable is defined that ranges from zero, when the structure is completely intact, to one, when a sample-spanning crack has formed. At low degrees of damage, defects occur at random, but after a certain time, they begin to occur close together: "localization" occurs [31]. Poon et al's dark field images of slow-fast sedimenting gels show initial formation of random defects and the slow growth of cracks very clearly [15]. They also show some universality in the rate of crack growth.

Many of the systems exhibiting delayed sedimentation are not brittle, so slow crack growth does not seem a plausible scenario. Perhaps the only plausible alternative is channeling [8], that has been observed mainly by chemical engineers and geophysicists.

Channelling

It has frequently been observed that the end of the slow phase of slow-fast sedimentation coincides with the formation of a sample-spanning fracture [3,5,30]. This can even be accompanied by the eruption of volcanos of material on the interface. Chemical engineers have extensively studied channeling for many years. A review can be found in reference [32].

The figure below is redrawn from Holdich and Butt [8]. It shows how channeling depends on volume fraction and strength of flocculation. So it is like a plane cut through the jamming phase diagram. The parallel is striking.

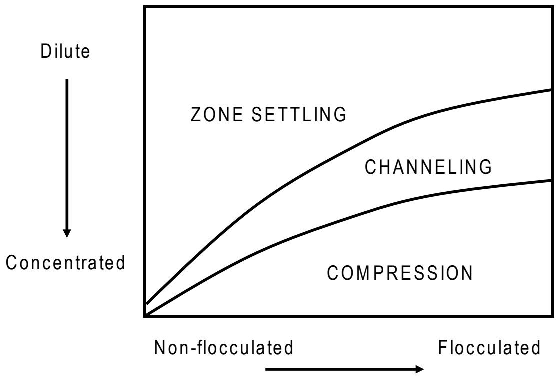

Figure 6 Conditions for channelling to occur during sedimentation as a function of volume fraction and strength of flocculation. Based on a diagram in ref. [8].

Zone settling occurs when the elastic contribution is negligible. Compression occurs when it is dominant. The compressive regime corresponds to "creeping sedimentation" described by Buscall [4] and studied by Kim et al [10].

Derec et al. [18] studied channeling during slow-fast sedimentation in strongly flocculated calcium carbonate. They show how the ratio between the rates of fast and slow sedimentation can be calculated using a simple model for flow inside and outside the channel.

It seems highly probable that channeling is intimately related to both delayed sedimentation and slow-fast sedimentation.

Aging

Both Verhaegh et al [28] and Kilfoil et al [19] observed the coarsening of their systems during the delay, using small angle light scattering and confocal microscopy. Buscall suggested [4] that the origin of delay is the thermally driven hopping of particles that coarsens the particle gel until a point that it loses connectivity. However, the dynamic light scattering measurements of both Verhaegh et al [28] and Poon et al [15] show that this appealing idea does not apply to their systems. Thermally driven coarsening is a diffusive process and so the angular dependence of the correlation function depends on the scattering vector, q, as q^{-2}. In fact, the angular variation of the correlation function scales as q^{-1}, indicating that the events causing rearrangement are ballistic and not diffusive. Cipelletti et al [25] observed the same dependence in their study of the physical aging of colloidal gels.

Physical aging occurs in a broad range of systems trapped far from equilibrium. Cipelletti et al. [33] showed that it occurs in several types of soft matter, including colloidal gels. The gel that they studied was carefully formulated to be neutrally buoyant, so gravitational effects were absent. The particles were dilute polystyrene latex, diameter = 10nm., $10^{-4} < \phi < 10^{-3}$. Coagulation was induced by adding 16mM $MgCl_2$. Gently twisting an old sample was sufficient to induce rapid shrinkage of the gel, presumably because the movement unstuck the sample from the wall, allowing the internal stresses to relax. It seems reasonable to assume that without density matching, the sample would have shown slow-fast sedimentation, like Allain's strongly flocculated calcium carbonate [3]. Their dynamic light scattering measurements show that the changes cannot be due to thermal hopping. They suggest that the aging is due to relaxation of internal stresses that are frozen-in during sample preparation. This mechanism seems to be quite general. In as far as this observation is true; the features of universal ageing must be part of a theory of delayed sedimentation. Cipelletti et al. [25] suggest that sintering of their polymer particles, due to the van de Waals' attraction, is a key part of the mechanism. This idea seems unlikely, because their observations agree in all possible points with those of Verhaegh et al. [28], who used hard silica particles, which did not sinter. Bouchaud and Pitard [34] have derived an improved theory to explain Cipelletti et al.'s results. They make the connection between the universal ageing, driven by internal stresses, and transient gelation. This direction looks very promising.

The yield time: a connection between rheology and delayed sedimentation

The idea that the rheology of a sample defines its sedimentation behaviour is very intuitive. However, no parameter that correlates robustly with the delay time has been found. De Kretser et al have recently reviewed the compressive rheology that is directly relevant to sedimentation [35]. However, they do not discuss time-dependent behaviour. On the other hand, in shear rheology, evidence is emerging for behaviour equivalent to delayed sedimentation: the "yield time" or delayed yield is observed in many weak solids close to the solid-liquid transition. Uhlherr et al. have shown the phenomenon very clearly for a number of systems [36]. Subsequently, Bauer et al. [37] and Gopalakrishnan and Zukoski [38] have shown similar results for surfactant crystals and model colloids, respectively. Even more recently, Caton and Baravian [39] have demonstrated apparently universal scaling between the yield time and the applied stress for a range of familiar yield stress fluids (ketchup, mustard …). Figure 7 shows some typical data.

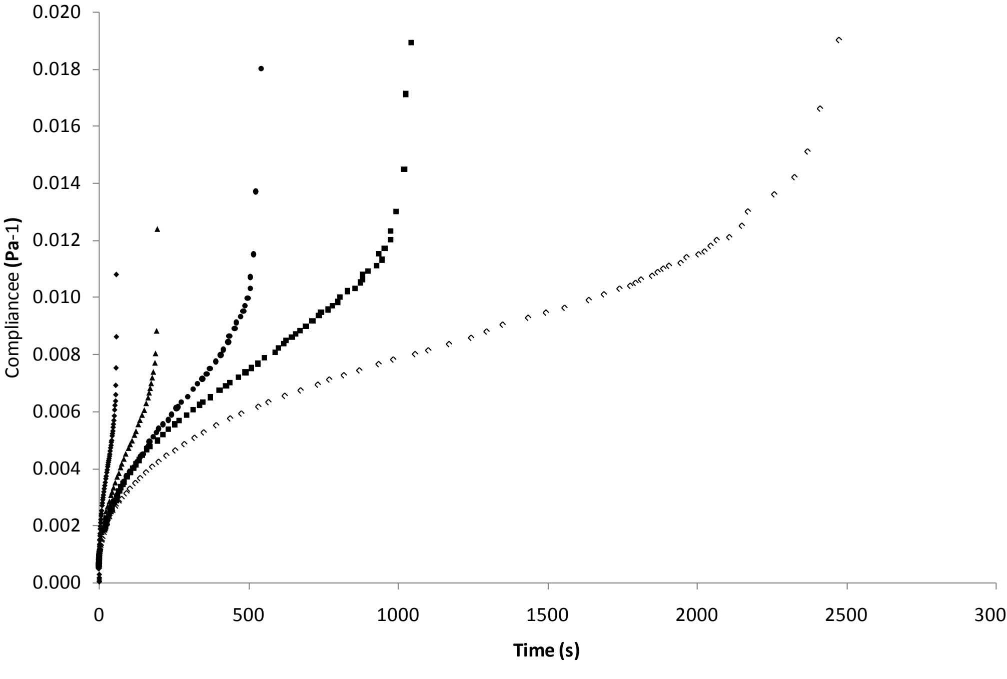

Figure 7 The yield time phenomenon. Creep curves measured with a vane geometry [40] for separate samples of yoghurt at stresses of: 400, 350, 300, 240, and 200Pa, going from left to right.

The generality of the yield time shows that system-specific theories are insufficient. Delayed sedimentation and delayed yield may share an explanation depending on damage accumulation, localization and finally a sudden increase in velocity, due to channeling/shear banding/fracture. The superficial analogy between the yield time and the delay time is very appealing, but it remains to be seen whether there is a deeper parallel and, if so, the exact nature of the relationship between the two. It would be very useful to compare measurements of the two phenomena for the same system.

Conclusions

Since Parker et al. first suggested delayed sedimentation as a paradigm, many aspects have become clearer:

- The phenomenon has been shown to be widespread.
- Delayed sedimentation is a subset of slow-fast sedimentation. The slow phase is invisible to the naked eye, due to low Darcy velocity, caused by the high continuous phase viscosity, high volume fraction and low density difference between phases.
- The effects of sample dimensions are complex and partially understood.
- Our new data shows how the delay time depends on the volume fraction of polymer. This parameter underlies the effects of the polymer's structure, molecular weight and concentration. This finding allows rational formulation.
- Our new data shows that the delay time scales with gravitational stress, induced by centrifugation. This result suggests a method for accelerated shelf life testing.
- The end of delay is not flow-driven, since often fast sedimentation starts after only an imperceptible amount of sedimentation has occurred.
- Restucturing during delay is not due to diffusion, as light scattering shows a q^{-1} dependence on scattering angle, not the q^{-2} dependence expected for diffusive dynamics.
- The variables controlling delayed sedimentation are the same as those in the jamming scenario for attractive colloids [27]. Delayed sedimentation occurs at the border separating jammed and unjammed states.

Although we still seem to be some way from a theory connecting all the relevant variables to the delay time, some of the pieces of the puzzle are falling into place. A major remaining difficulty is defining the roles played by aging and creep fracture. It is clear that both play central roles in certain systems, but we still do not have a theory that defines the relevant conditions. In particular: during the delay, are we waiting a) for the system to change into a suitable state (aging) or b) waiting for slow changes to occur in an unchanging system (creep fracture)? Are both essential? It seems that some young systems are too "soft" to support channels and must age into a state that allows channels or fractures to grow. On the other hand, it seems that slow growth of these channels or fractures can also set the time before fast sedimentation begins. The extreme sensitivity to initial conditions, such as whether the container is round or square, looks like a fracture-related phenomenon.

Delayed sedimentation only occurs over a narrow range of parameter space, so it might be thought to be insignificant. In fact, its importance to the formulator is disproportionately large, because the formulation process naturally selects samples with delay. Those that undergo immediate sedimentation are quickly eliminated as unstable. Those with permanent sedimentation are often too structured to fulfill their function: they are insufficiently pumpable, pourable, printable, etc. Therefore, candidate formulations that are "just stable enough" naturally fulfill the maxim "make the delay time longer than the shelf life". In conclusion: rational formulation of colloidal dispersions that are gravitationally stable requires understanding of this fascinating phenomenon.

Acknowledgements

I dedicate this article to Catherine Allain, who died recently. Her elegant contributions to this area deserve wide recognition. My thanks go to Florence Vigouroux, Christian Miniou and Maryvonne Moal, who made previously unpublished measurements cited here.

References

1. A. Parker, P. A. Gunning, K. Ng, and M. M. Robins, Food Hydrocolloids **9,** 333 (1995).
2. F. Concha and R. Burger, Miner. Metall. Process. **20,** 57 (2003).
3. C. Allain, M. Cloitre, and M. Wafra, Phys. Rev. Lett. **74,** 1478 (1995).
4. R. Buscall, Colloids Surf. **43,** 33 (1990).
5. L. Starrs, W. C. K. Poon, D. J. Hibberd, and M. M. Robins, J. Phys. : Condens. Matter **14,** 2485 (2002).
6. F. M. Auzerais, R. Jackson, and W. B. Russel, J. Fluid Mech. **195,** 437 (1988).
7. F. M. Auzerais, R. Jackson, W. B. Russel, and W. F. Murphy, J. Fluid Mech. **221,** 613 (1990).
8. R. G. Holdich and G. Butt, Miner. Eng. **9,** 115 (1996).
9. R. Buscall and L. R. White, J. Chem. Soc. , Faraday Trans. 1 **83,** 873 (1987).
10. C. Kim *et al.*, Phys. Rev. Lett. **99,** 028303-028303/4 (2007).
11. R. Tuinier and C. G. de Kruif, J. Colloid Interface Sci. **218,** 201 (1999).
12. G. Velez *et al.*, J. Agric. Food Chem. **51,** 265 (2003).
13. P. Manoj *et al.*, J. Coll. Inter. Sci. **207,** 283 (1998).
14. M. A. Faers *et al.*, Colloids Surf. A **288,** 170 (2006).
15. W. C. K. Poon *et al.*, Faraday Discuss. **112,** 143 (1999).
16. L. Bergstrom, C. H. Schilling, and I. A. Aksay, J. Am. Ceram. Soc. **75,** 3305 (1992).
17. K. E. Davis, W. B. Russel, and W. J. Glantschnig, J. Chem. Soc. , Faraday Trans. **87,** 411 (1991).
18. C. Derec, D. Senis, L. Talini, and C. Allain, Phys. Rev. E **67,** 062401-062401/4 (2003).
19. M. L. Kilfoil, E. E. Pashkovski, J. A. Masters, and D. A. Weitz, Philos. Trans. R. Soc. London, Ser. A **361,** 753 (2003).
20. O. Mengual *et al.* Talanta, **50**, 445-456. (1999).
21. L. Bergstroem, J. Chem. Soc., Faraday Trans. **88,** 3201 (1992).
22. S. M. Ilett, A. Orrock, W. C. K. Poon, and P. N. Pusey, Phys. Rev. E, **51,** 1344 (1995).
23. D. Senis and C. Allain, Phys. Rev. E **55,** 7797 (1997).
24. A. S. Michaels and J. C. Bolger, Ind. Eng. Chem. Fundam. **1,** 24 (1962).
25. L. Cipelletti, S. Manley, R. C. Ball, and D. A. Weitz, Phys. Rev. Lett. **84,** 2275 (2000).
26. A. J. Liu and S. R. Nagel (eds.), *Jamming and rheology: constrained dynamics on microscopic and macroscopic scales*, Taylor and Francis, London (2001).

27. V. Trappe *et al.*, Nature, **411,** 772 (2001).
28. N. A. M. Verhaegh, D. Asnaghi, and H. N. W. Lekkerkerker, Physica A **264,** 64 (1999).
29. A. Guarino, S. Ciliberto, and A. Garcimartin, Europhys. Lett. **47,** 456 (1999).
30. S. Manley, J. M. Skotheim, L. Mahadevan, and D. A. Weitz, Phys. Rev. Lett. **94,** 218302-218302/4 (2005).
31. A. Garcimartin, A. Guarino, L. Bellon, and S. Ciliberto, Phys. Rev. Lett. **79,** 3202 (1997).
32. N. Kurta, PhD thesis, RMIT University, Australia, (2006).
33. L. Cipelletti *et al.*, Faraday Discuss. **123,** 423 (2003).
34. J. P. Bouchaud and E. Pitard, Eur. Phys. J. E **6,** 231 (2001).
35. R. G. de Kretser, D. V. Boger, and P. J. Scales, Rheol. Rev. 125 (2003).
36. P. H. T. Uhlherr *et al.*, J. Non-Newtonian Fluid Mech. **125,** 101 (2005).
37. T. Bauer, J. Oberdisse, and L. Ramos, Phys. Rev. Lett. **97,** 258303-258303/4 (2006).
38. V. Gopalakrishnan and C. F. Zukoski, J. Rheol. **51,** 623 (2007).
39. F. Caton and C. Baravian, Rheologica Acta **23,** 85 (2008).
40. C. Baravian, A. Lalante, and A. Parker, Appl. Rheol. **12,** 81 (2002).

Chapter 4

Elasticity Due to Semiflexible Protein Assemblies near the Critical Gel Concentration and Beyond

First, we apply to gelatin gels a recent model, which predicts the percolation concentration of semi-flexible protein assemblies. We show that it can also be applied to calculate the percolation concentration of helices in gelatin gels, up to a constant of order unity. Second, we show that Morse' model for the elasticity of semiflexible fibril systems describes well the elasticity of gelatin gels far above the critical gel concentration, without any adjustable parameters. Third, we show that these models, for the low and high concentration regimes, can be tied together using a harmonic mean approximation

E. van der Linden and A. Parker, Langmuir, **21**, 9792 (2005)

Introduction

Recently, Joly-Duhamel et al. [1] reported that the elastic modulus of gelatin gels can be described in terms of the concentration of triple helices. Their data convincingly point to the existence of a critical gelation concentration of helices, c_p, also referred to as the (critical) percolation concentration. Below this concentration, no elasticity is detectable. Above this concentration, roughly up to about $2c_p$, the elastic modulus, G', was found to scale according to $G' \approx (c - c_p)^t$, with c the concentration of helices in the system and $t = 1.9$, the exponent for so-called isotropic force percolation. The critical gel concentration was briefly discussed and related to Philipse's recent theory [2] for the critical percolation concentration of rigid rods. The data of Joly-Duhamel et al. [1] summarize a concise and very thoroughly conducted experimental investigation on gelatin gelation.

We have three aims. The first is to point to a recently introduced model, which successfully predicts the percolation concentration of semiflexible protein assemblies in terms of the mesoscopic properties of the fibrils [3]. We show that it can also be applied to calculate the percolation concentration of helices in gelatin gels, up to a constant of order unity. The second aim is to show that an existing model by Morse [4] for the elasticity of semiflexible fibril systems, using the concept of deflection length, introduced by Odijk [5], can be successfully applied to describe the elasticity of gelatin gels far beyond the critical gel concentration, without any adjustable parameters. The third aim is to show that the low concentration regime, $c < 2c_p$, and the high concentration regime, $c >> c_p$ (though still in the isotropic regime), can be tied together using a harmonic mean approximation as suggested by Joly-Duhamel et al. [1], but now using the before mentioned alternative descriptions. The results presented here are envisioned to be applicable to all semi-flexible fibril systems, including amyloid type materials [6] and carbon nanotubes [7].

Discussion

Philipse [2] derived an expression for the percolation concentration of perfectly rigid rod gels. He found $c_p = \alpha D_0/L$, where α is a constant of order unity, related to the number of contacts between neighboring rods, D_0 is the thickness of the rod and L is its length. In the expression given by Philipse, and in what follows, the unit of concentration is volume fraction.

For semi-flexible fibrils, the result of Philipse must be modified to take into account the finite value of the persistence length, L_p, of the fibril. For that case, Veerman et al. [3] have reported $c_p = \alpha D_0/L_p$. They showed that this expression successfully describes the gelation of three different classes of semi-flexible protein assemblies [8]. The value of α is of order one in the case when a gel is formed by contact between rigid rods. In the case of semi-flexible rods, also $\alpha = 1$ has been reported [3]. However, in the case of gelatin, a gel may form when there is less than one contact per helix, due to flexible coils connecting the ends of different helices. The latter is very likely since each helix has two dangling coils attached to it [1] (in total there are three dangling ends, which all have an equal chance to be part of another helix). Thus, the chance of having one contact with another helix at gelation has to be increased by a factor of about 3, compared to the case of rigid rods without dangling coils. Thus, for gelatin gels built up by semi-flexible helices, one would expect $c_p = (\alpha/3).D_0/L_p$. Using $L_p = 170$ nm for gelatin helices [1] and $D_0 = 1.5$ nm, this implies $c_p = 0.0029\alpha$. To test this result, we extracted the data points of G' versus helix concentration from the paper of Joly-Duhamel et al. [1], using the program Un-Scan-It from Silk Scientific Corp. We then determined the critical helix concentration from these data. We converted the data of Joly-Duhamel et al. [1] from g/cm^3 into volume fraction using the reported conversion factor of 1.44, the density of gelatin [1]. We found that the critical helix volume fraction $c_p = 0.0028$. This implies $\alpha \approx 1$, i.e., of order unity as expected. Hence, a theoretical estimate for the critical percolation concentration in gelatin gels leads to $c_p = (\alpha/3)D_0/L_p$ and is in good agreement with experiment. Fitting the extracted data of G' up to about $c = 2c$ yields that the G' near the percolation threshold is given by:

$$G_{perc} = 2 \times 10^7 \left(c - c_p\right)^{1.94}$$

(with R^2 of 0.99). The prefactor of 2×10^7 is the only adjustable parameter for the percolation regime. The other parameters come directly from the percolation model.

For $c >> c_p$ (although remaining in the isotropic regime), many elasticity models have been suggested. In the paper of Joly-Duhamel et al. [1], some of them are reviewed, but these models do not completely satisfactorily describe the experiments on gelatin. Most of the existing models do not take into account the flexibility of the fibrils. The difficulties lie in: 1) finding a satisfactory description of how the deformation of a test fibril affects the deformation of its neighbors and 2) describing how the presence of neighboring fibrils affects the shape and deformation of a test fibril and the corresponding deformation energy. Often, one calculates the bending energy of a test fibril on the basis of its persistence length and the wavelength of deformation. However, Odijk [5] has shown that for a semi-flexible fibril another length scale becomes relevant when such a fibril is confined within a tube of diameter d. This length scale is termed the deflection length, L_{def}, given by [5] $L_{\mathrm{def}} = d^{2/3} L_p^{1/3}$. In the case of an isotropic solution of fibrils in the semidilute regime, any test fibril will feel the presence of its neighbors. In fact, the test fibril may be presumed to be effectively confined to a tube that results from the presence of the neighboring fibrils. One therefore expects that the deflection length should enter the problem of elasticity of an isotropic solution of semi-flexible fibrils in the semi-dilute regime. Defining the number of fibrils per unit of volume by v, and considering the assumption that G' is based on the number of contacts per fibril with their respective surrounding tubes, one writes $G' \approx vkTL/L_{\mathrm{def}}$ [9]. This expression is dependent on the specific type of deformation, but remains the same up to a factor of order unity [4]. To arrive at the dependency of G' on concentration, one should know how L_{def} depends on concentration and, equivalently, how the diameter of the effective tube, d, depends on the concentration of fibrils. Morse [4] and also Frey et al. [9] have given the relation between d and the concentration of fibrils. Their expression makes use of another relevant length scale, the mesh size, ξ_m, of the system. This parameter is related to the number (per unit area) of fibril intersections with an arbitrary test plane, which is given by $1/\xi_m^2$. This number per unit area is related, in turn, to the number of fibrils per unit volume, v, according to $\xi_m^2 = 3/vL$ [9]. According to a scaling argument of Frey et al. [9] and the analysis of Morse [4], one has $d \approx \xi_m^2/L_{def}$, implying $d \approx 3/(vLL_{def})$. Combining the latter equation with $L_{def} = d^{2/3}L_p^{1/3}$, one may solve for L_{def} and find $L_{def} = (3L_p^{1/2}/vL)^{2/5}$. Using $v = 4c/\pi D_0^2 L$ and substituting L_{def} into the expression for G', we find for the high concentration end of G', i.e., G' high

$$G'_{high} = \beta kT\left(D_0^2/4\right)^{-7/5}\left(9L_p\right)^{-1/5}c^{7/5}$$

with β a constant of order unity. Using the values for D_0 and L_p, this yields for gelatin:

$$G'_{high} = (4.2 \times 10^5)\beta c^{1.4}$$

Fitting this expression to the high concentration end of the extracted data, we find $\beta = 2.5$, an eminently reasonable value. The high concentration regime for elasticity can thus be described by a model discussed by Frey et al. [9] and by Morse [4], using the deflection length [5] as an essential element.

To model the transition between the low and high concentration regimes, Joly-Duhamel et al. [1] suggested a harmonic mean approximation, i.e.

$$1/G'_{total} = 1/G'_{perc} + 1/G'_{high}$$

This approximation can be justified as follows. First, the approximation is valid when one assumes that the overall elastic response of the system results from two contributions which act like two springs connected in series. The harmonic mean approximation is, in contrast, to a sum approximation, i.e., $G'_{total} = G'_{perc} + G'_{high}$, which assumes the analogy of two springs in parallel. In the series analogy, a hypothetical strain on one type of spring will always be detected by a (different) neighboring type of spring, since both springs are connected, whereas in the parallel analogue, such a connectivity between different springs is assumed not to exist. The gelatin system above the percolation concentration exhibits a percolating structure with concomitant elastic response (spring type 1) to a given strain. At high enough concentrations, the system will also show an elastic response (in a presumably affine manner) to a given strain, due to the deformation of the tubes (spring type 2). If any deformation of the tube is felt by a neighboring tube (as is implied in effect by the assumption of affine deformation of the tubes), such a deformation will certainly be also felt by the neighboring percolating structure (spring type 1), and vice versa. Thus the two types of springs in the gelatin system exhibit connectivity, and will therefore act together as if they were in series, justifying the harmonic approximation. An additional arguments in favor of this approximation is that it yields the correct limit for $c > c_p$, whereas the sum approximation, i.e., $G'_{total} = G'_{perc} + G'_{high}$, does not yield $G'_{total} = 0$ for $c = c_p$.

To fit experimental data to eq 4, eqs 1 and 3 are used, with optimization of the prefactor in eq 1 and the factor β in eq 3. Figure 1 shows a good fit of the combined theories to the data over the entire range of helix concentrations. This fit was obtained by adjusting β to 5 for G'_{high} and leaving the pre-factor G'_{perc} unchanged.

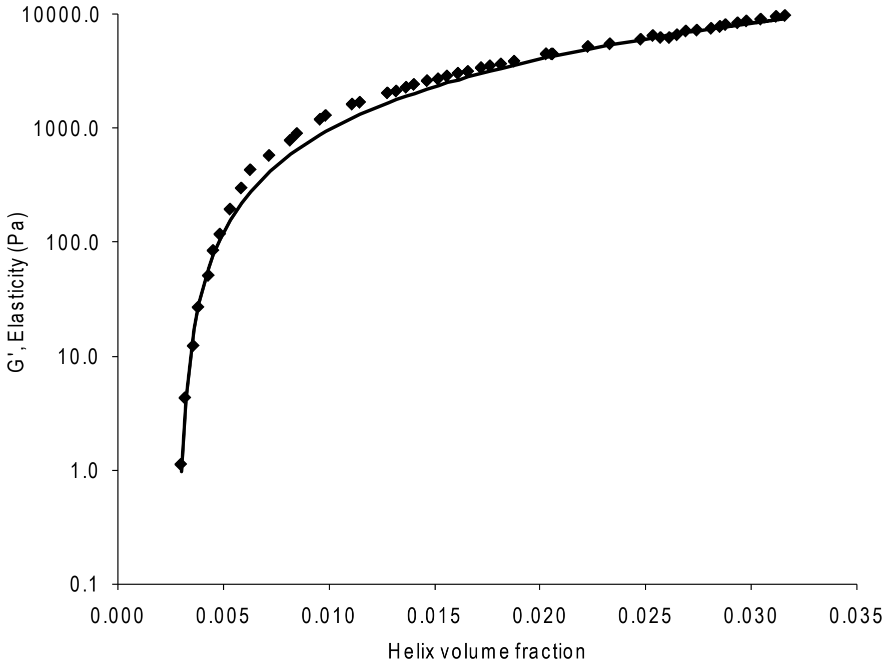

Figure 1. Elasticity of a gelatin gel as a function of the helix concentration. Symbols are experimental data from ref 1. Line is a least squares fit to eq 4.

We conclude that the elasticity of gelatin gels over a broad range of gelatin concentrations can be described in a single model that combines a percolation model, for low helix concentrations, with a model based on the deflection length, for high helix concentrations. The model gives an improved view of the physics underlying the elasticity of a gelatin gel over its entire concentration range. It should be applicable to any system of semi-flexible rods over a large concentration range.

This model for *G'* could be further tested by considering its frequency dependence. If one assumes for the high concentration range that the tube model yields the dominant contribution, one expects a $\omega^{3/4}$ dependency at these higher concentrations [10]. For gelatin, the ω dependence has an exponent in the range of 0.62-0.72 at the gel point, in accordance with percolation theory, but this exponent does exhibit a dependence on concentration and gel history within the accessed experimental ω range of 0.01-1 [10,11]. The exponent can even become as low as 0.25, deeper into the gel region [11], within the frequency range of 0.01-1. If this low value persists at higher frequencies, it would imply a dominant relaxation mode different from the one proposed in the tube model, resulting from the more complex connectivity that exists within the gelatin system.

Acknowledgments We want to thank the referees for their comments.

References

1. C. Joly-Duhamel, D. Hellio, A. Ajdari, and M. Djabourov, Langmuir **18,** 7158 (2002).
2. A. P. Philipse, Langmuir **12,** 5971 (1996).

3. C. Veerman, H. Ruis, L. M. C. Sagis, and E. van der Linden, Biomacromolecules **3,** 869 (2002).

4. D. C. Morse, Phys. Rev. E **63,** 031502-031502/22 (2001).

5. T. Odijk, Macromolecules **16,** 1340 (1983).

6. W. S. Gosal, A. H. Clark, P. D. A. Pudney, and S. B. Ross-Murphy, Langmuir **18,** 7174 (2002).

7. O. Regev, P. N. B. ElKati, J. Loos, and C. E. Koning, Adv. Mater. **16,** 248 (2004).

8. L. M. C. Sagis, C. Veerman, and E. van der Linden, Langmuir **20,** 924 (2004).

9. E. Frey, K. Kroy, and J. Wilhelm, Adv. Struct. Biol. **5,** 135 (1998).

10. C. Michon, G. Cuvelier, and B. Launay, Rheol. Acta **32,** 94 (1993).

11. M. Djabourov, J. Leblond, and P. Papon, Journal de Physique **49,** 333 (1988).

Chapter 5

Scaling in the dynamics of gelatin gels

Gelatin gels never reach equilibrium. The storage modulus increases linearly in log(time) after some initial time, typically one hour. This behaviour, which is characteristic of physical ageing, makes it hard to define the gelation concentration, gelation temperature and gel melting temperature in a non-arbitrary way. For instance, after slight heating close to the gelation temperature certain gels melt, but then reform several hours later. The gelation kinetics for all temperatures, concentrations, molecular weight distributions and times can be parameterised by forming master curves in log(elasticity)/log(time) space. The effects of temperature and concentration are independent. For concentrations between 7.5 and 100 g/kg we find no evidence for a critical gelation concentration. For a given sample, all the data can be fit using a single critical temperature, which shows the characteristics of the critical temperature of a second order phase transition. There are two regimes with different critical exponents. We call these "close-to-critical" and "far-from-critical". Cuts made in a gel during the close-to-critical regime heal, whereas cuts made once a gel is in the far-from-critical regime do not heal. The effects of temperature jumps in the two regimes are qualitatively different. Both show scaling properties. These results are discussed in the context of the physics of out of equilibrium systems

V. Normand and A. Parker, *Proc. 3^rd^ Int. Symp. Food Rheol. Structure*, eds. P. Fischer, I. Marti and E.J. Windhab, 185 (2003).

Introduction

The gelation of gelatin has been extensively studied for many years. In a classic study [1], Te Nijenhuis showed how complex the kinetics were after temperature jumps. In 1997, Ross-Murphy summarised current ideas about the gelation of gelatin [2]. We will show that our results are in disagreement with several of these.

Durand and co-workers were the first to take a scaling approach to the gelation kinetics of weak gels [3-5]. They showed that master curves could be formed for both β-lactoglobulin and κ-carrageenan. Inspired by this work, Normand et al. [6] showed that the gelation kinetics of a wide range of gelatin gels (six molecular weight distributions, four temperatures, three concentrations) could be superposed on an arbitrary reference curve by shifting them in log(storage modulus)/log(time) space. The majority of the data could be fit by a linear dependence of the shift factors on temperature, concentration and molecular weight distribution. However, it was clear that a different scaling was required when the temperature was too high or the concentration too low. For reasons that we explain below, we call these two regimes “far-from-critical” and “close-to-critical”, respectively.

Experimental

Measurements were made with a Physica MCR 300 rheometer, fitted with a 5cm diameter, 2° angle cone and plate geometry. Oscillatory measurements were made at a frequency of 1Hz and a strain of 2%, which is in the linear viscoelastic range. The gelatin was a 250 Bloom acid pigskin supplied by DGF. Solutions were prepared as previously [6, 7] by heating for 30min at 60°C while gently stirring.

Results and discussion

Isothermal gelation

We have made two helpful observations:

1) When measuring gelation at 1Hz, the storage and loss moduli are equal when the storage modulus is close to 1Pa. This gives a simple definition of the gel point, close to frequency independent estimates [8].

2) At long times (typically after 1h for concentrations above 30g/kg and temperatures below 20°C), the storage modulus evolves at a constant rate as a function of log(time). This behaviour is the defining characteristic of physical ageing [9]. It is a good marker for when steady state has been reached.

Fig. 1 shows some typical data for the storage modulus as a function of time at temperatures close to the gelation temperature, in the close-to-critical regime. Note how strongly the kinetics depend on the temperature.

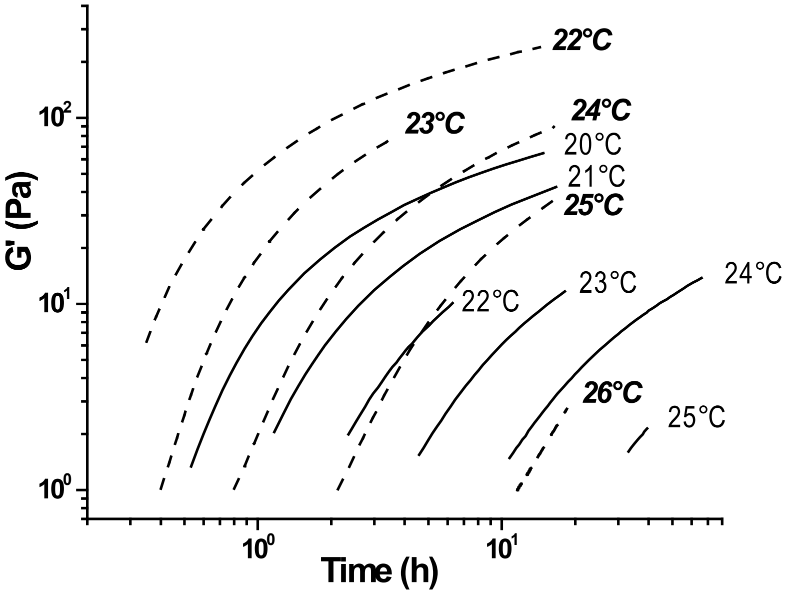

Figure 1 Typical gelation kinetics in the close-to-critical regime. Concentrations: Solid lines: 20g/kg, Dashed lines: 40g/kg.

We improve on the previous work [6] by superposing these data without using an arbitrary reference curve. Instead, we use an equation inspired by the theory of critical phenomena [10]. Close to the critical point of a second order phase transition, critical slowing down occurs. The relaxation time, τ, diverges as: $\tau \propto |X_c - X|^n$, with X a system variable (temperature or concentration), X_c its critical value and n an exponent. We fit the data in fig. 2 to the formula:

$$\frac{G(t)}{\varepsilon^{\alpha}(c-c_c)^{\mu}} = g\left(\frac{t}{\varepsilon^{\beta}(c-c_c)^{\nu}}\right) \qquad (1)$$

where ε is the reduced temperature, $\varepsilon = 1 - \frac{T}{T_c}$ (T in °C), c is the concentration expressed as weight fraction, t is time and g(x) is a scaling function defining the shape of the master-curve. The four exponents and the critical concentration, c_c, are fitting parameters.

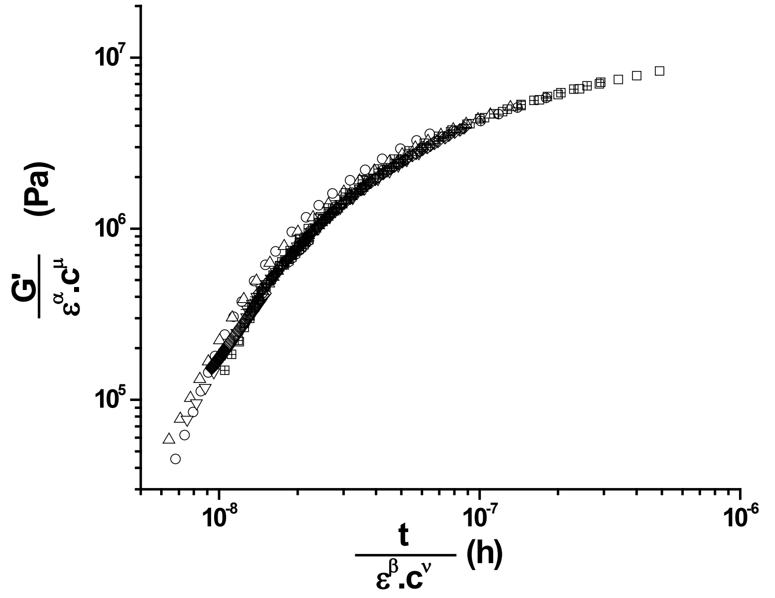

Figure 2 Critical scaling of data in fig. 1. Solid symbols 20g/kg, open symbols 40g/kg. Best fit values in eq. (1) were: $\alpha = 3.23 \pm 0.09$, $\beta = -9.30 \pm 0.13$, $\mu = 2.3$, $\nu = -2.6$, $c_c = 0$, $T_c = 35.8°C$.

Fig. 2 shows that the best fit of eq. (1) to the data in fig. 1 gives an excellent collapse onto a single curve. Data for concentrations between 7.5 and 100g/kg also fell onto the same curve. Setting the critical concentration, c_c, to zero gave the best fit, implying that the critical gelation concentration is much lower than the lowest concentration studied. We argue that this approach is the only non-arbitrary way of determining the critical gelation concentration, as it is time-independent.

This scaling only works at temperatures close to T_c. Fig. 3 shows that typical data at low temperature first follow the master curve in fig. 2 and then gelation suddenly slows down, causing a systematic deviation below the master curve.

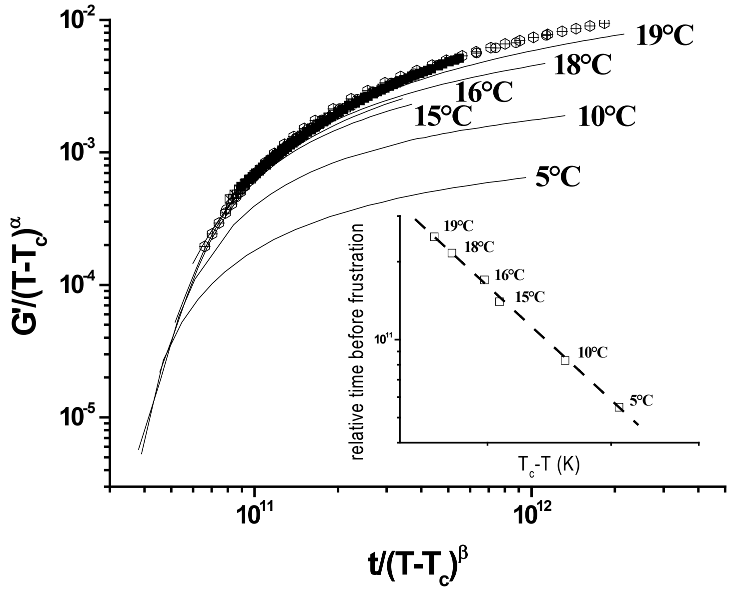

Figure 3 Deviation of cold-aged gels from master curve in fig. 2. Inset shows that time at which deviation occurs scales with the distance from the critical temperature.

The inset to fig. 3 shows that the critical time at which the deviation occurs scales with the distance from T_c. Fig. 4 shows this data, together with some for the critical time as a function of concentration.

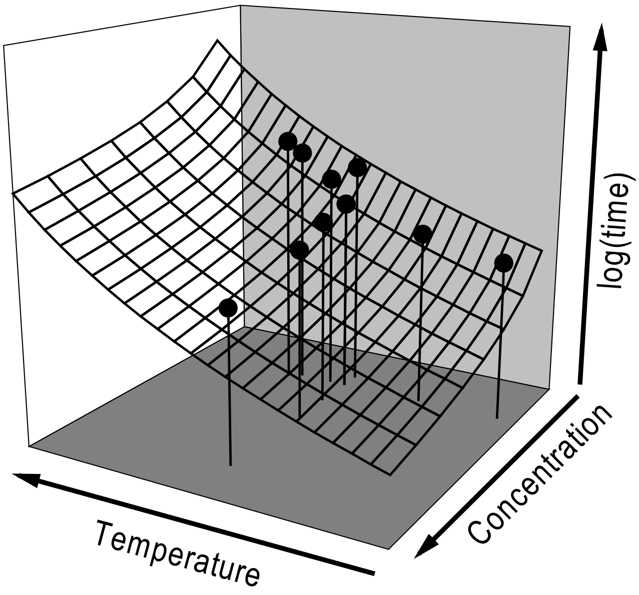

Figure 4 Surface defining the critical time that separates the close-to-critical (below the surface) and far-from-critical regimes (above).

Eq. (1) collapses the data in the far-from-critical regime too (data not shown), using the same critical temperature as for the close-to-critical regime, but different exponents. In particular, the time exponent of the reduced temperature, β, falls from about -9 to close to -2, quantifying the observation that gels which are far-from-critical evolve much more slowly than when they are close-to-critical.

Gelatin gels close to and far from critical are not only differentiated by their scaling exponents. There is also a correlation with a very simple observation that was reported previously [6]: a gel is cut in two and the pieces placed back together. A cut made when the gel is close to critical will heal, whereas a cut made when it is far from critical will not.

Effects of temperature jumps

Fig. 5 shows a spectacular and previously unreported effect that occurs after sudden heating in the close-to-critical regime. Gels were first aged at 15°C for up to 1 hour and then heated to 24°C, well below the critical temperature. These gels melted very quickly after heating, but then re-formed some hours later, before a sample aged entirely at 24°C had started to gel.

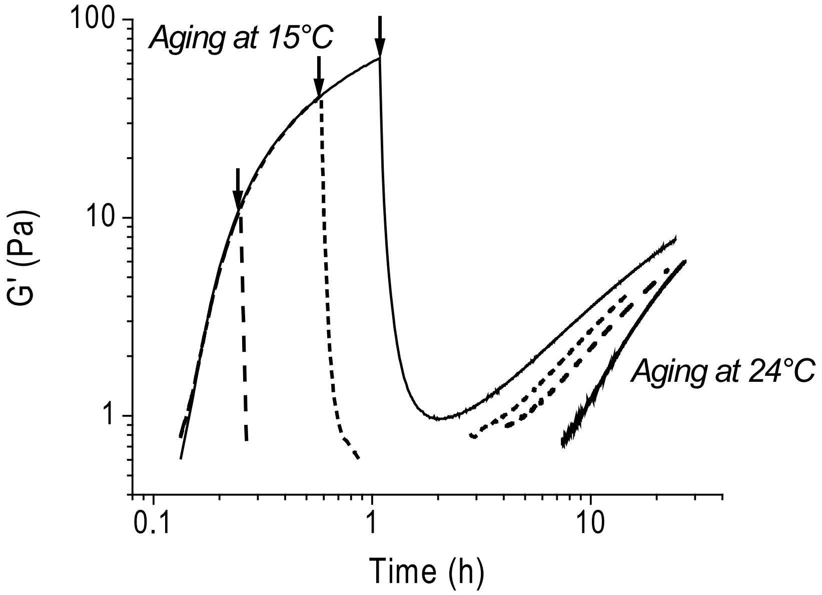

Figure 5 Effect of sudden heating in the close-to-critical regime. The gel labelled isothermal was aged at 24°C. The others were aged for different times at 15°C and then heated to 24°C. Arrows indicate the time at which the gel was heated.

Heating these gels melted them. Then a wait as long as several hours was needed to discover that they re-gelled. On heating, these gels fall below the percolation threshold, but retain some structure. These data illustrate how hard it is to define the gel melting temperature.

Fig. 6 shows that the kinetics for the cold aged gels can be shifted onto that of the hot aged gel, using linear axes. Some time after heating a cold aged gel, it acts exactly like a gel which has been hot aged for longer.

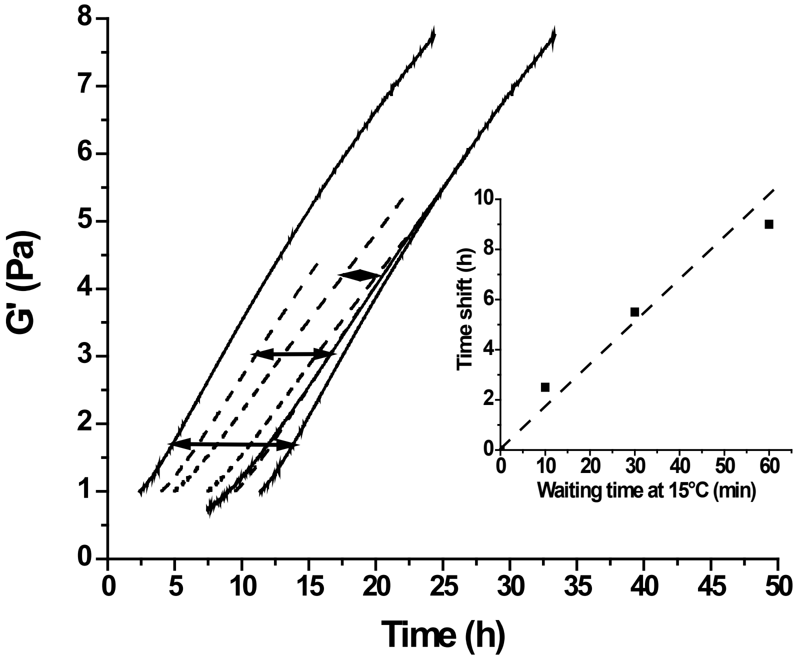

Figure 6 Superposition of data after sudden heating in the close-to-critical regime (fig. 5) by shifting in time.

Fig. 7 shows the kinetics after sudden heating in the far-from-critical regime. The storage modulus first falls rapidly, but then starts to rise again. At long times, there is a constant gap (in log time) between the hot aged and cold aged gels, so that the data for the cold-aged gel can be superposed on that for the hot-aged sample by shifting along the log(time) axis. The cold aged gel shows accelerated ageing.

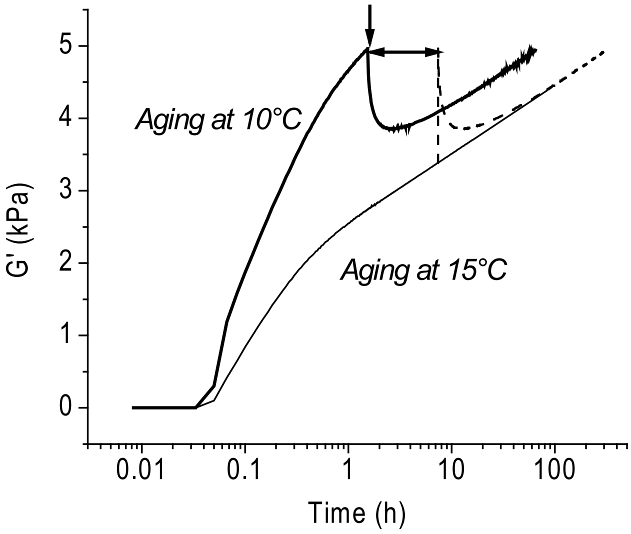

Fig. 7 Effect of sudden heating in the far-from-critical regime.

Cooling/Heating cycles

The complex effects of memory in gelatin gels are best observed using the following two stage protocol: 1) cooling at a constant rate from above T_c to below it and then heating at the same rate. This gives the reference curve. 2) Cooling and heating in the same way, but stopping once or twice during the cooling. Fig. 8 shows the results for experiments heating and cooling at 0.2Kmin^{-1} with one stop. Fig. 9 shows the difference between the reference curve and the curve with a stop.

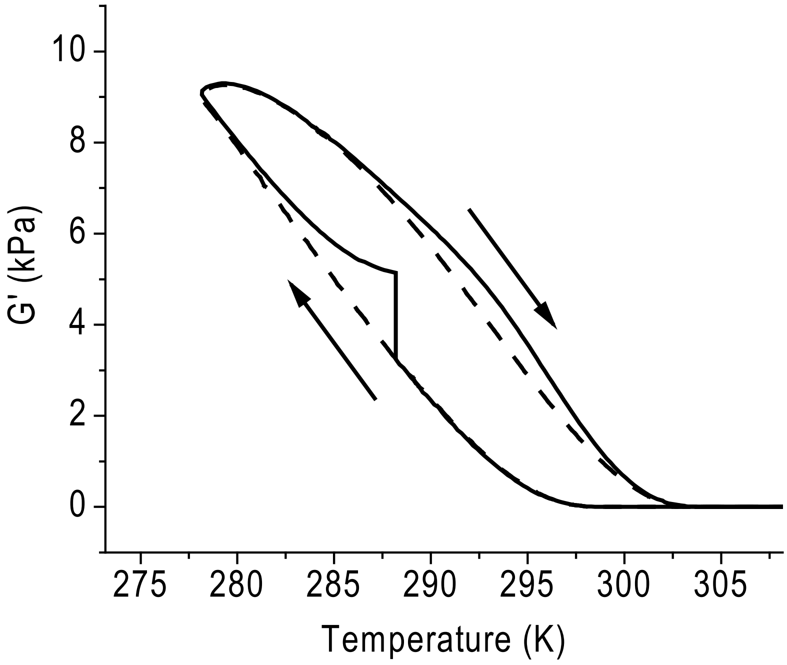

Figure 8 Storage modulus during cooling/heating cycle. Dashed line - no stop. Solid line – stop for 1h at 15°C.

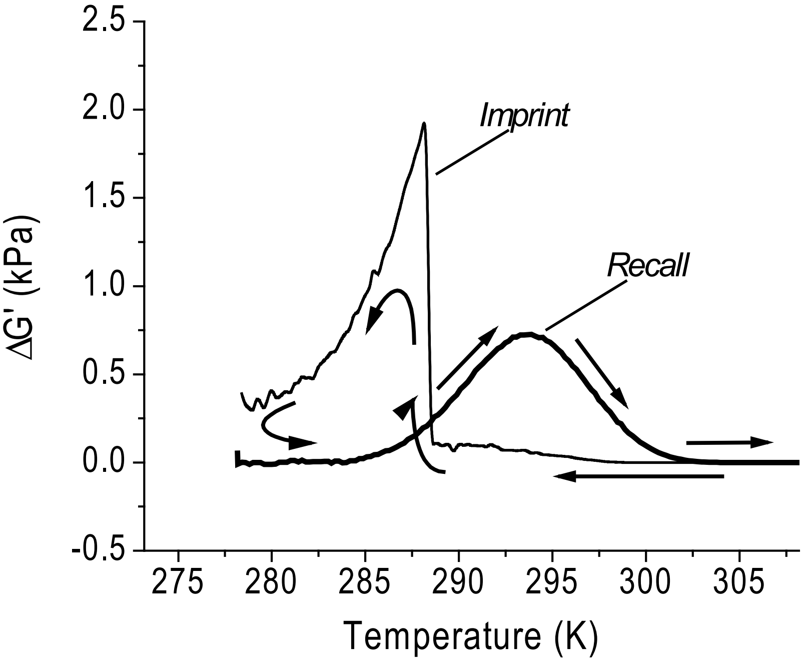

Figure 9 Difference in storage modulus between stop and no stop data in fig. 8.

Fig. 10 shows that if cooling is stopped twice, the gel has two corresponding melting peaks on heating. We also find that the result with two stops is just the sum of the data for two separate stops.

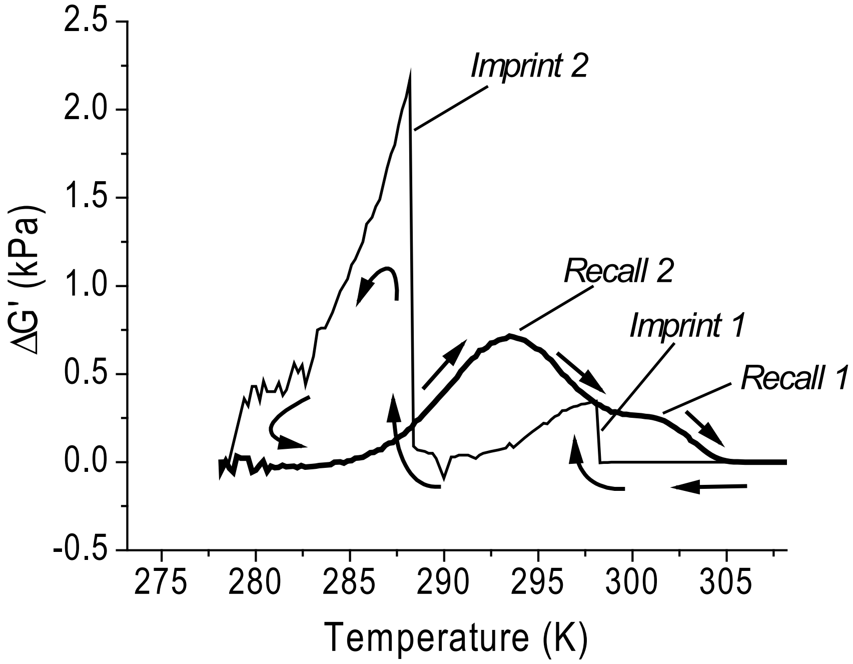

Figure 10 Difference in storage modulus between stop and no stop data for cooling/heating cycle with two stops 1h at 15°C and 2h at 25°C.

The key points are: i) at low temperature the sample shows the same behaviour with or without stopping - it temporarily forgets its past, ii) on heating the sample remembers that it stopped, which causes a melting peak to appear about 10°C above the stopping temperature(s). This kind of behaviour has been seen only twice before, but in completely different systems: the canonical result is for the magnetic response of spin glasses [11]. The second is in the dielectric response of a polymer glass [12]. For spin glasses the "melting" peak occurs exactly at the stopping temperature. For our gels the melting peak occurs 10°C higher. Fig. 11 shows that this is an effect of heating rate. We heat gels at different rates and plot the temperature difference between stopping and melting. The lower the heating rate, the smaller the difference. The linear extrapolations suggest that the melting and stopping temperatures would coincide at a heating rate of less than 5 × 10^{-5} Kmin^{-1}. We think that this difference between spin glasses and gelatin gels (as well as Bellon et al.'s polymer glass [12]) is just due to the much slower dynamics of the gels.

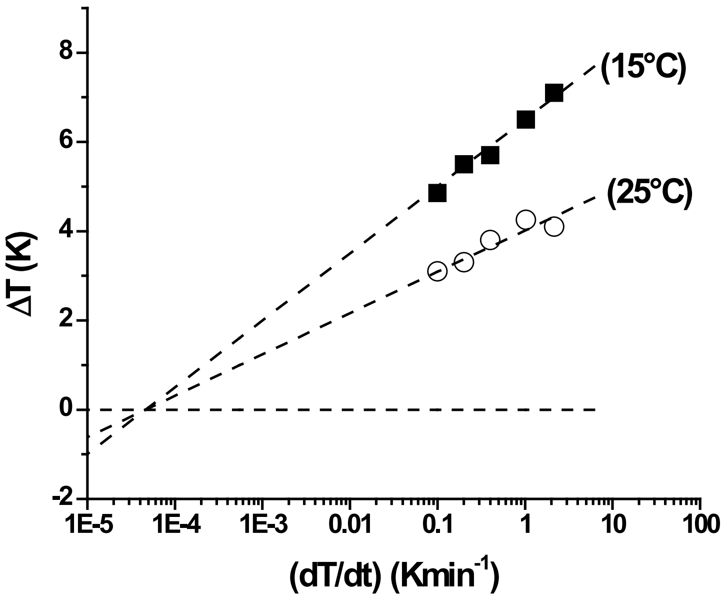

Figure 11 Effect of heating rate on temperature difference between stopping temperature and temperature of melting peak for stopping temperatures of 15°C and 25°C.

Conclusions

We have shown that a scaling approach greatly simplifies the description of the complex dynamics of gelatin gels. Even at a phenomenological level, we feel that our observation that there are two regimes with different scaling laws is extremely useful. All gels start in the close-to-critical regime and pass at some critical time into the far-from-critical regime. As well as the scaling of the gelation kinetics, the regime also determines the effects of temperature jumps and the healing/non-healing of cuts.

Returning to Ross-Murphy's review [2], we contest his assertion that "It is well accepted that a sample which does not gel at 20°C will gel at 4°C." We argue that "does not gel" is too strong a statement. For our sample, the fit to eq. (1) shows that the gelation kinetics are about 500 times slower at 20°C than 4°C, so a sample that gels in one day at 4°C will take one and half years to gel at 20°C.

We have shown that temperature and concentration have equivalent effects on the gelation of gelatin. This same idea has recently become very popular for yield stress fluids and other "jammed" systems [13, 14]. However, the jamming paradigm has only been applied to time-independent systems until now. In systems that age, time matters. Scaling the whole time evolution seems a promising approach to understanding, or at least parametrizing, the effects of time on systems jammed far from equilibrium.

We have shown that gelatin gels undergo physical ageing and that their dynamics has analogies with that of other out of equilibrium systems. We think that exploring these analogies will lead to better understanding of gelatin and other thermoreversible gels.

Acknowledgements

We thank Jorge Kurchan, Sergio Ciliberto and Eric Vincent for their explanations of the physics of out of equilibrium systems.

References

1. K. te Nijenhuis, Coll. Polym. Sci. **259**, 1017 (1981).
2. S. B. Ross-Murphy, Imaging Sci. J. **45**, 205 (1997).
3. J. C. Gimel, D. Durand, and T. Nicolai, Macromolecules **27**, 583 (1994).
4. P. Aymard, T. Nicolai, and D. Durand, Macromolecules **32**, 2542 (1999).
5. V. Meunier, T. Nicolai, D. Durand, and A. Parker, Macromolecules **32**, 2610 (1999).
6. V. Normand, S. Muller, J. C. Ravey, and A. Parker, Macromolecules **33**, 1063 (2000).
7. V. Normand and J. C. Ravey, Rheol. Acta **36**, 610 (1997).
8. C. Michon, G. Cuvelier, and B. Launay, Rheol. Acta **32**, 94 (1993).
9. L. C. E. Struick, *Physical aging in amorphous polymers*, Elsevier, Houston (1978).
10. H. E. Stanley, *Introduction to phase transitions and critical phenomena.* Clarendon Press, Oxford (1971).
11. K. Jonason *et al.*, Phys. Rev. Lett. **81**, 3243 (1998).
12. L. Bellon, S. Ciliberto, and C. Laroche, Europhys. Lett. **51**, 551 (2000).
13. A. J. Liu and S. R. Nagel, Nature **396**, 21 (1998).
14. V. Trappe *et al.*, Nature **411**, 772 (2001).

Chapter 6

Spin glass-like dynamics of gelatin gels

We measure the elasticity of thermoreversible gelatin gels during slow cool and heat cycles, with and without stops. The responses, which are measures of the system energy, show the same memory and rejuvenation (chaos) effects as spin glasses. At constant temperature, all gels reach an aging regime, where their responses decrease linearly in log(time) like spin glasses. The memory effects after temperature jumps are also similar to those of spin glasses. We suggest that the parallels between the two systems are due to their temperature-dependant, rugged, hierarchical energy landscapes. Gelatin gels act like "colloidal spin glasses", so the relation between mesoscopic dynamics and macroscopic behavior should be measurable experimentally.

Submitted to:

Physical Review E

Introduction

An intriguingly wide range of complex systems show similar non-equilibrium dynamics, despite their completely different microscopic organization. Examples include spin glasses [1,2], glassy polymers [3,4], granular media [5] and type II superconductors [6]. The dynamics are characterized by aging - a slow decrease in the rate of dynamical processes after a quench - and a rich variety of memory effects. Key questions are: What mesoscopic features are necessary and sufficient for the occurrence of these phenomena? How do the mesoscopic dynamics control the macroscopic behavior? They can only be answered if the full range of systems that exhibit these dynamics is explored.

We show several remarkable parallels between the dynamics of a thermoreversible polymer gel and spin glasses. Our central finding is an almost exact reproduction of the memory and rejuvenation effects found in spin glasses by Jonason et al. [7]. Thermoreversible gels are an important class of soft condensed matter with intricate dynamics [8-10]. They are clearly trapped far from equilibrium. In fact, more than twenty years ago de Gennes remarked that such weakly cross-linked gels “should show some of the intricacy of the glass transitions” [11]. This suggestion has not been tested previously. We do so here using the archetypal thermoreversible gel made from gelatin [12], a helix-forming protein.

Gelatin is obtained by degrading collagen [12]. When gelatin solutions are cooled below about 40°C, the separate disordered chains start to combine and re-form portions of collagen triple helix, eventually forming a gel [12]. The ordered phase is the collagen helix, so, in contrast to spin glasses [13], there is no “temperature chaos”: the equilibrium correlations are negligibly temperature-dependent.

The triple helix of collagen melts close to 37°C; the exact value depends strongly on the experimental protocol [14]. Previous studies of gelatin gels have found melting temperatures between 17°C and 31°C [9,15,16]. The result depends on the molecular weight, concentration, time and temperature of aging and the heating rate. Until recently, the elasticity of gelatin gels was interpreted using the theory of rubber elasticity. The developing collagen helices were considered as crosslinks between the remaining polymer coils. The elasticity was assumed to be due to the loss of entropy as these cross-linked coils were stretched. This point of view had problems. For instance, Chatellier et al. [17] showed for a range of gelatin concentrations and quench temperatures that gelation always occurred at a critical concentration of helices. This conceptual problem was recently solved by Joly-Duhamel et al. [15]. They showed: 1) the elasticity is uniquely determined by the helix concentration, independent of the gelatin concentration, 2) the sol-gel transition is a percolation threshold, with the helix concentration as the control parameter. The relationship between elasticity and helix concentration is well explained by assuming that the elasticity is due to interactions between the stiff rods formed by the helices [18]. This work clarifies the origin of the gels’ elasticity, but does not help to understand the complex effects of time and temperature on their dynamics [8-10].

In our previous work [10,19], we showed that gelatin gels display two of the key features of glassy systems:

1) The mechanical response has peaks at two widely separated frequencies, which is typical of structural glasses (see, for instance, [20]).
2) At constant temperature, and for aging times between one hour and six months, the elastic modulus of a broad range of gelatin gels increases as log(time). For glassy systems in general, the rate of physical aging [21] is proportional to $(\log(\text{time}))^{\zeta}$ with $\zeta \approx 1$ [22].

Following a quench, once each gelatin chain is involved in at least two helices, the system must become frustrated, due to the competition between neighbouring helices for the shared portions of non-helical chain. Frustration, the incompatibility of local and global energy minimization [23], is a key feature of glassy systems [24] and of complex systems in general [25].

Materials and methods

Measurements of linear viscoelasticity were made at 1Hz, as previously [10]. Data were reproducible to within a few per cent. The gelatin was a sample of 200 Bloom (an industry standard for the gel strength) extracted by treating pig skin with acid. Solutions were prepared as previously [10] by heating for 30min at 60°C while gently stirring.

Results

When a glassy system is cooled below the glass transition temperature, T_g, equilibrium is never reached. The system properties then depend on the time spent below T_g. We equate the glass transition temperature with the gelation temperature of gelatin gels. In general, glassy systems remember their past history. Often this memory is simply cumulative. The key characteristic that distinguishes spin glasses from most other glassy systems is that memory can be lost *temporarily* on cooling to lower temperatures (rejuvenation) [7]. This effect is best observed using a two-stage protocol [7]: A non-perturbing alternating field is applied (magnetic for spin glasses, mechanical for gels). The response (magnetic susceptibility for spin glasses, elastic modulus, G’, for gels) is a measure of the system’s energy. It is measured whilst: 1) cooling at a constant rate from above T_g to below it and then heating at the same rate. This gives the reference curve. 2) Cooling and heating in the same way, but stopping during cooling. A stop imprints a memory on the system. Recall of this memory is shown by a higher response during the heating step, at a temperature close to the stopping temperature.

Figure 1 shows the results for a gelatin gel with one stop (1a and 1c) and two stops (1b and 1d). Figures 1a and 1b show the raw data. Figures 1c and 1d show the difference between the experiments with and without stops ($\Delta G' = G' - G'_{\text{ref}}$). This latter presentation makes clear the position and size of the broad memory recall peaks.

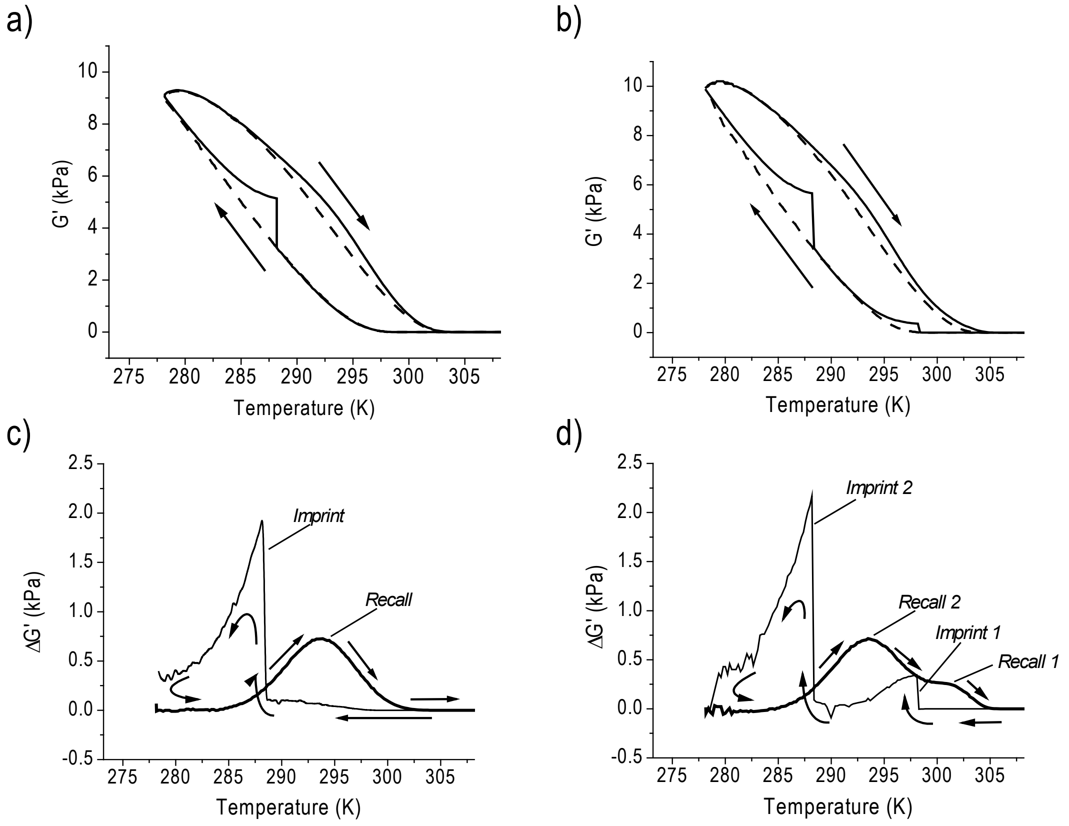

Figure 1 Memory and rejuvenation effects for gelatin gels. Top row shows storage modulus G' measured during cooling and then heating at 0.2Kmin^{-1}*. The dashed line is the reference curve measured during continuous cooling and heating. The solid line is the result with stopping. Bottom row shows the difference between the reference curve and the stopping curve. The thin line is for cooling and the bold line for heating. On the left one stop: 1h at 15°C. On the right two stops: 2h at 25°C and 1h at 15°C. Gelatin concentration = 100g/kg.*

Remarkably, these results are essentially identical to those for spin glasses in that:
i) At low temperature the sample shows the same behavior with or without stopping: it has apparently forgotten its past. In spin glasses, this was originally called the chaos effect [13]. The term rejuvenation is now preferred [26], since it not clear that temperature chaos is the origin of the observed effect.
ii) On heating, the sample remembers that it stopped, causing a memory recall peak to appear close to the stopping temperature.

For both spin glasses and gelatin gels, the balance between memory and rejuvenation depends on both the duration of the stop and its distance from the minimum temperature of the loop [27]. When the stop is long and close to the minimum temperature of the loop, memory dominates and the influence of the stop persists at the lowest temperatures. When the stop is short and far above the minimum temperature, then rejuvenation dominates and the stop has no influence at the lowest temperatures.

A further similarity between gelatin gels and spin glasses [28] is that the response after two stops at well separated temperatures is just the sum of the responses to the stops alone: separate imprinting of memories leads to separate recall.

These results show that spin glasses and gelatin gels share energy landscapes with similar structures. In terms of the energy landscape, the requirements for memory and rejuvenation effects are well known: it must be rugged, hierarchical and temperature dependant [26,29]. Since there is no common feature in the microscopic details of the two systems, a deeper question is: what real space structures give rise to such similar energy landscapes? We return to this below.

A significant difference between spin glasses and gelatin gels/polymer glasses is that for spin glasses the memory recall peak occurs very close to the stopping temperature [7]. For gelatin gels, and Bellon et al.'s polymer glass [3], the memory recall peak occurs about 10°C higher. We now show that this difference is simply due to the different timescales of organization. A series of gels were cooled at the same rate and with the same stop, but heated at different rates. Figure 2 shows the difference between the stopping temperature and the memory recall peak as a function of the heating rate.

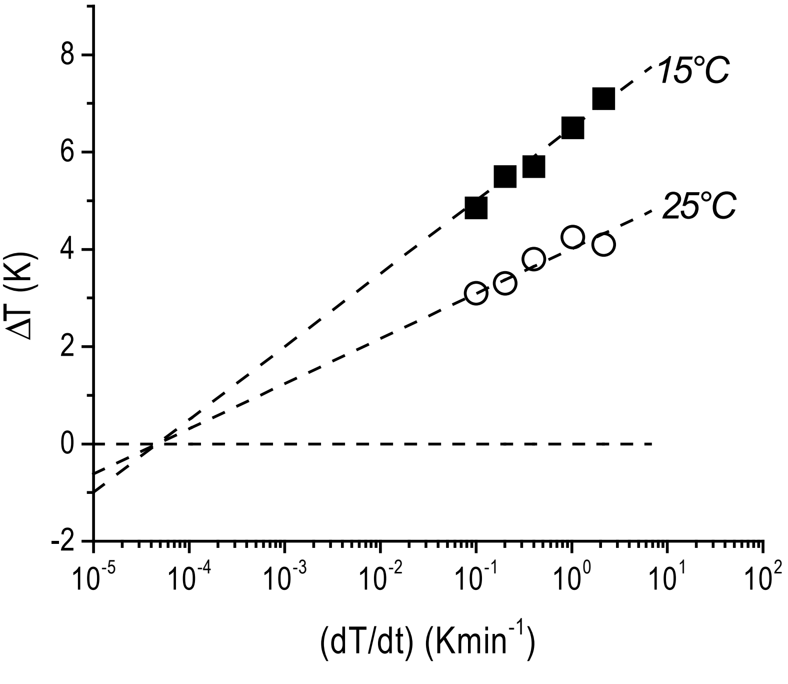

Figure 2 Effect of heating rate on the difference between the stopping temperature and the temperature of the memory recall peak for stopping temperatures of 15°C and 25°C. Extrapolations are by eye.

Lower heating rates lead to smaller temperature differences. The arbitrary extrapolations suggest that the melting and stopping temperatures would coincide at a heating rate of less than 5 x 10^{-5} Kmin^{-1}. Bächinger et al. showed that the rate of collagen helix formation is close to 10ms per amino acid [30]. In a spin glass, the typical spin flip time is about 1ps. Thus, the extrapolated cooling rate for gelatin gels corresponds to 10^8 events/K, whereas for spin glasses it is typically 10^{14} events/K [7]. By this measure the experimental cooling rates for gelatin gels are many orders of magnitude faster than for spin glasses, plausibly explaining the observed difference in behavior.

Complex memory effects occur in both real [31,32] and simulated [33] spin glasses after temperature jumps. Such non-monotonic responses were first observed by Kovacs in polymer glasses [34]. We find that gelatin gels show similar behaviour. Figure 3 shows two striking memory effects that occur when gels are suddenly heated after aging.

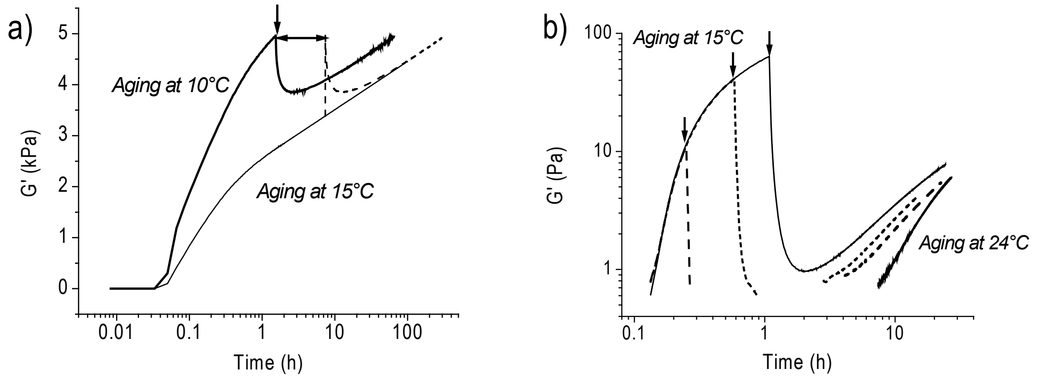

Figure 3 Kovacs-like memory effects on heating aged gels a) Heating after long aging. The gel was aged for 1 hour at 10°C and then rapidly heated to 15°C. Vertical arrow indicates the time of the temperature jump. The horizontal arrow and dotted curve indicate that cold aging has the same effect as hot aging for longer. c = 67g/kg. b) Heating soon after gelation. Three gels were aged for different times at 15°C and then heated to 24°C at a time indicated by the arrows. The heated gels first melt and then re-form at some later time, before a gel aged only at 24°C. c = 20g/kg.

This phenomenon is similar to the Kovacs effect, first seen in polymer glasses [34] and subsequently in simulated spin glasses [35] and granular media [5]. After temperature jumps, the system response is not monotonic, but makes an excursion (the Kovacs hump) before reaching steady state at the new temperature. In spin glasses and gelatin gels, the equilibrium state is never reached, so the transition is between two aging regimes. The Kovacs effect in gelatin gels and spin glasses are not identical. Fig 3a shows that in gelatin after an upward temperature jump the gel behaves as though it was *older* than a gel aged solely at the *higher* temperature. In spin glasses the shift is in the opposite direction [32,35].

Discussion and Conclusions

We observed physical aging for a wide range of gels in our previous work [19], but did not connect it to the relevant non-equilibrium physics. Here we have shown that, after a certain time at constant temperature, whatever a sample's history, it will reach the aging regime and remain there. Since physical aging is a key feature of such a diverse range of complex systems, its cause must be quite general. Anderson et al. [25] argue that sufficient ingredients are 1) frustration and 2) strain, caused by random configurations not satisfying all the constraints imposed by local interactions.

Up to now, the only explanation for the complex effects of temperature on the dynamics of gelatin gels has been an intuitive appeal to defects in the helices [36]. However, defects are not adequate to explain the phenomena observed here. We offer a more plausible picture. Below the gelation temperature, helices start to form, but the system quickly becomes frustrated, once growing helices connect all the random coils. Competition occurs between the enthalpically favourable formation of compact helices and the unfavourable increase in entropic stretch of the attached portions of random coil. Thus, the system must eventually reach a marginally stable state, where the opposing forces are in balance, on average. In such frustrated systems, the equilibrium state is irrelevant to the dynamics. The system is trapped in long lived metastable states. When the temperature is decreased, the stretch in the coils decreases, so fast helix growth occurs, until a new marginally stable state is reached. When the temperature is increased, the coils are over-stretched and so they pull helices apart until marginal stability is reached.

In the marginal state, helix formation and destruction are not symmetrical. Once a new piece of helix has formed, the cooperativity of the helix-coil transition (see, for instance, Flory [37]) ensures that the chances of reversal are so small as to be effectively irreversible. This effective irreversibility is generic to complex systems and is the origin of physical aging [25].

If this class of model does apply to gelatin gels, then they too should exhibit intermittent dynamics, which could be measured directly. Intermittent dynamics have been demonstrated experimentally by noise measurements in a polymer glass showing memory and rejuvenation [38] and in both real [39] and simulated [40] spin glasses. Therefore, we predict that they also occur in gelatin gels.

Given the parallels that we have described, we suggest that gelatin can serve as a "colloidal spin glass", in the same way as experimental studies of colloidal dispersions have clarified aspects of atomic physics (see, for example, [41]). Gelatin gels have several clear advantages over spin glasses: the longer length scale and slower time scale of gelatin gels allow the slow dynamics to be probed directly, using light scattering [42], so the connection between the mesoscopic and macroscopic dynamics can be measured directly. We expect more detailed comparisons of spin glasses and gelatin gels to lead to better understanding of universality and specificity in these and other glassy systems.

We thank Jorge Kurchan, Erik van der Linden and Sergio Ciliberto for their suggestions. The advice of Eric Vincent and Paolo Sibani was invaluable.

References

1. P. Nordblad, J. Phys. : Condens. Matter **16,** S715 (2004).
2. E. Vincent, Lect. Notes Phys. **716,** 7 (2007).
3. L. Bellon, S. Ciliberto, and C. Laroche, Europhys. Lett. **51,** 551 (2000).
4. L. Bellon, S. Ciliberto, and C. Laroche, Eur. Phys. J. B **25,** 223 (2002).
5. C. Josserand, A. V. Tkachenko, D. M. Mueth, and H. M. Jaeger, Phys. Rev. Lett. **85,** 3632 (2000).
6. M. Nicodemi and H. J. Jensen, J. Phys. A **34,** 8425 (2001).
7. K. Jonason *et al.*, Phys. Rev. Lett. **81,** 3243 (1998).
8. C. Michon, G. Cuvelier, P. Relkin, and B. Launay, Int. J. Biol. Macromol. **20,** 259 (1997).
9. K. te Nijenhuis, Coll. Polym. Sci. **259,** 522 (1981).
10. V. Normand, S. Muller, J. C. Ravey, and A. Parker, Macromolecules **33,** 1063 (2000).
11. P. G. De Gennes, *Scaling Concepts in Polymer Physics*, Cornell University Press, 324 (1979).
12. T. R. Keenan, in *Kirk-Othmer Encycl. Chem. Technol. (5th Ed.)*, **12**, 436 (2005).
13. A. J. Bray and M. A. Moore, Phys. Rev. Lett. **58,** 57 (1987).
14. E. Leikina, M. V. Mertts, N. Kuznetsova, and S. Leikin, PNAS **99,** 1314 (2002).
15. C. Joly-Duhamel, D. Hellio, A. Ajdari, and M. Djabourov, Langmuir **18,** 7158 (2002).
16. J. E. Eldridge and J. D. Ferry, J. Phys. Chem. **58,** 992 (1954).
17. J. Y. Chatellier, D. Durand, and J. R. Emery, Int. J. Biol. Macromol. **7,** 311 (1985).
18. E. van der Linden and A. Parker, Langmuir **21,** 9792 (2005).
19. V. Normand and J. C. Ravey, Rheol. Acta **36,** 610 (1997).
20. W. Kob, in *Soft and fragile matter*, Edited by M. E. Cates and M. R. Evans, SUSSP and IOP, Bristol (2000).
21. L. C. E. Struik, *Physical Aging in Amorphous Polymers and Other Materials* Elsevier, New York and Amsterdam, 242 (1978).
22. J. P. Bouchaud, L. Cugliandolo, J. Kurchan, and M. Mézard, in *Spin-glasses and random fields*, Edited by A. P. Young, World Scientific, Singapore (1998).
23. D. Sherrington, Physica D **107,** 117 (1997).
24. G. Tarjus and D. Kivelson in *Jamming and rheology*, Edited by A. J. Liu and S. R. Nagel, Taylor Francis, London and New York, 20 (2001).
25. P. E. Anderson, H. J. Jensen, L. P. Oliveira, and P. Sibani, Complexity **10,** 49 (2004).
26. J. P. Bouchaud, in *Soft and fragile matter*, Edited by M. E. Cates and M. R. Evans (SUSSP and IOP, Bristol (2000).
27. K. Jonason *et al.*, Eur. Phys. J. B **13,** 99 (2000).
28. R. Mathieu *et al.*, Phys. Rev. B **65,** 012411 (2001).
29. P. Sibani and H. J. Jensen, Europhys. Lett. **69,** 563 (2005).
30. H. P. Bachinger *et al.*, Eur. J. Biochem. **106,** 619 (1980).
31. V. Dupuis *et al.*, Phys. Rev. B **64,** 174204 (2001).
32. M. Sasaki, V. Dupuis, J. P. Bouchaud, and E. Vincent, Eur. Phys. J. B **29,** 469 (2002).
33. H. Takayama and K. Hukushima, J. Phys. Soc. Jpn. **71,** 3003 (2002).
34. A. J. Kovacs, Adv. Poly. Sci. **3,** 394 (1963).
35. T. Komori, H. Yoshino, and H. Takayama, J. Phys. Soc. Jpn. **69,** 228 (2000).

36. K. te Nijenhuis, Coll. Polym. Sci. **259,** 1017 (1981).
37. P. J. Flory, *Statistical Mechanics of chain molecules*, Wiley, New York, (1969).
38. L. Buisson, S. Ciliberto, and A. Garcimartin, Europhys. Lett. **63,** 603 (2003).
39. P. Sibani, G. F. Rodriguez, and G. G. Kenning, Phys. Rev. B **74,** 224407 (2006).
40. P. Sibani and H. J. Jensen, J. Stat. Mech. : Theor. Exp. P10013 (2004).
41. H. Lekkerkerker, in *Soft and Fragile Matter*, Edited by M. E. Cates and M. R. Evans, Institute of Physics Publishing, 305 (2000).
42. A. Duri, H. Bissig, V. Trappe, and L. Cipelletti, Phys. Rev. E **72,** 051401 (2005).

Chapter 7

Thixotropic gels and dairy desserts

Rapid thixotropic recovery is an important factor in the production of multi-layer dairy desserts. Therefore the thixotropy of gels and model dairy desserts containing ι-carrageenan has been studied. The results of thixotropic recovery in a rheometer after: i) gelation under shear and ii) subsequent cold shearing are compared for aqueous gels, milk gels and model dairy desserts. These measurements are compared with the recovery of samples sheared during processing on a pilot plant. Thixotropic recovery was never complete and appeared to be divided into a fast and a slow component. Both the viscosity during gelation under shear and the kinetics of recovery can be scaled, so that results for all shear rates form a single master-curve. For cold shearing of already formed gels the maturation time before shearing was not a significant factor for aqueous or milk gels, but caused significant differences in the final texture of model dairy desserts treated on a pilot plant.

A. Parker and G. Tilly, *Gums and Stabilisers in the Food Industry*, **7**, 393-401, 1994.

Introduction

It is common knowledge in the food industry that ι-carrageenan gels are thixotropic. However, there is very little published scientific study of this phenomenon [1, 2]. As a result of its thixotropy, ι-carrageenan is used in multi-layer dairy desserts, which are very popular in France, and increasingly in other Western European countries. In their simplest form, these desserts consist of two layers: the lower layer is a coffee or chocolate flavoured carrageenan milk gel also containing starch, whilst the upper layer consists of a whipped dairy topping. In France such desserts are typically called “Liegeois” or “Viennois” after the ice-cream sundaes from which they were derived. The market trend is towards even more sophisticated forms with three, or even four, different layers.

Liegeois-type desserts are manufactured as follows:

i) The dry ingredients for the lower layer are dispersed in cold milk and then heat-treated (pasteurised or sterilised). Their dissolution is complete at this stage.
ii) The hot solution is cooled to 10°C in a plate or tubular heat exchanger, causing gelation of the carrageenan, which thus occurs under shear.
iii) Traditionally, this cold gel is held in a storage tank whilst slowly stirring, for between 30 minutes to 2 hours, depending on the availability of a filling line, Experience shows that a dessert of uniform quality cannot be produced if the storage time is too variable, as the gel’s properties change quickly under these conditions.
iv) The cold gel is pumped into the final 100mL pot.
v) A few seconds later, the topping is pumped onto the gel layer.

In the short time between stages iv) and v), the lower layer must undergo sufficient thixotropic recovery to support the topping, without deforming. An uneven interface between the two layers is a readily observed default, since the pots are always transparent. The relevant rheological property of the lower layer is its ability to support a weight, i.e. its elasticity, not its viscosity.

The term thixotropy has been defined by Mewis [3] as follows: “There is rather general agreement to call thixotropy the continuous decrease of apparent viscosity with time under shear and the subsequent recovery of viscosity when flow is discontinued”. However, this definition does not exclude elastic effects, although few studies of elastic recovery after shearing have been made (see, for example ref. 4). Mewis [3] continues: “thixotropy becomes noticeable in viscoelastic materials when the stress or viscosity recovery after cessation of flow takes more time than the stress relaxation”.

In this study, the thixotropic behaviour of ι-carrageenan in dairy desserts has been examined and compared with that of gels in water and milk, to discover whether the particular properties of these products are intrinsic to ι-carrageenan, or only occur when it is incorporated into a complex dessert formulation.

Materials and methods

The ι-carrageenan was an industrial sample obtained from Sanofi Bio-Industries, France and was used as received. Its ionic form was 70% potassium/30% sodium. The degree of contamination by the kappa form was estimated using the elasticity/temperature relationship of a 5gL^{-1} solution in 0.2M NaCl, as suggested by Parker *et al.* [5]. Whilst the kappa form was not completely absent it did not constitute more than 3% of the total carrageenan, according to the calibration curve in ref. 5.

Water gels were prepared containing 5gkg^{-1} of carrageenan in 0.15M NaCl; giving an ionic strength close to that of milk. Milk gels were prepared containing 3gkg^{-1} carrageenan in reconstituted semi-skim milk. A model liegeois was made containing: 85% (by weight) skim milk, 12.7% sucrose, 2% modified starch and 0.3% (3gkg^{-1}) ι-carrageenan.

All rheological measurements were made with a Carri-Med CS 100 controlled stress rheometer, fitted with a 4cm, 2° stainless steel cone. In order to simulate a heat exchanger, it was necessary to cool samples through the sol-gel transition whilst shearing them at a constant rate. It was found that with a sufficiently fast PC (16MHz 386SX), the feedback loop for stress control was so tight that the requested shear rate was respected to within a few tenths of a per cent. Oscillatory measurements were made at 1Hz, using a strain of 14%, which was in the linear viscoelasticity region. The gap was set to the correct value at 10°C before starting each experiment.

Solutions were prepared by heating at 90°C for 30 minutes and then placed in the measurement system, pre-heated to 65°C. In all cases, the sample remained for 10 minutes at this temperature before cooling began. For gelation under shear, the chosen shear rate was applied during this time. The sample was then cooled to 10°C in 15 minutes (Results obtained by cooling in 30 minutes were not significantly different). As soon as 10°C was attained, stress was no longer applied to the sample and the cone stopped. Low deformation oscillatory measurements began immediately, the first measurement being taken between 5 and 10 seconds after the cone had stopped. Measurements were usually taken for 10 minutes. Cold shearing of samples was carried out by shearing for 2 minutes at 600s^{-1} at a variable time after gelation under the same shear rate. Subsequent thixotropic recovery was followed in the same way as for the samples gelled under shear.

Results and discussion

Given the lack of published data for the thixotropy of ι-carrageenan, relatively complete results are presented for the water gels, whilst only the aspects relevant to multi-layer desserts are shown for the milk gels and model dairy desserts.

Water gel: effect of shear during gelation

Fig. 1 shows the viscosity as a function of temperature during cooling from 65°C to 10°C, at different shear rates. As might be expected, the viscosity is greatly reduced by increasing the shear rate. However, the temperature at which the viscosity increases sharply, 56°C, is close to the gel point measured by oscillation, and does not vary with the shear rate. In this case, the application of shear neither retards nor accelerates gelation.

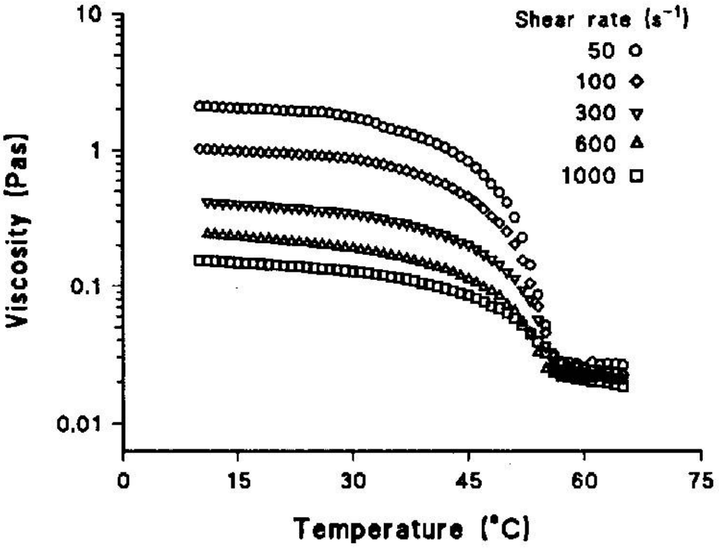

Fig. 1 Water gel: Effect of shear rate on the viscosity during gelation under shear

This point is better illustrated by fig. 2, in which the data in fig. I are compared with the shear modulus, using the reduced variable, X_{red} , given by:

$$X_{red} = \frac{X_T - X_{65}}{X_{10} - X_{65}}$$

where X_T is the shear modulus or viscosity at temperature *T*. Surprisingly, the reduced viscosities fall onto a single master curve (similar results were found for milk gels, but are not shown). It is very clear from this graph that the temperature at which the viscosity begins to rise does not depend on shear rate. Further interpretation of this interesting result is not obvious, but it might be taken to show that ι-carrageenan gels only contain one type of structure whose extent of formation is gradually reduced as the imposed shear rate is increased. The only effect of increasing the shear rate is to reduce the scale of the viscosity change.

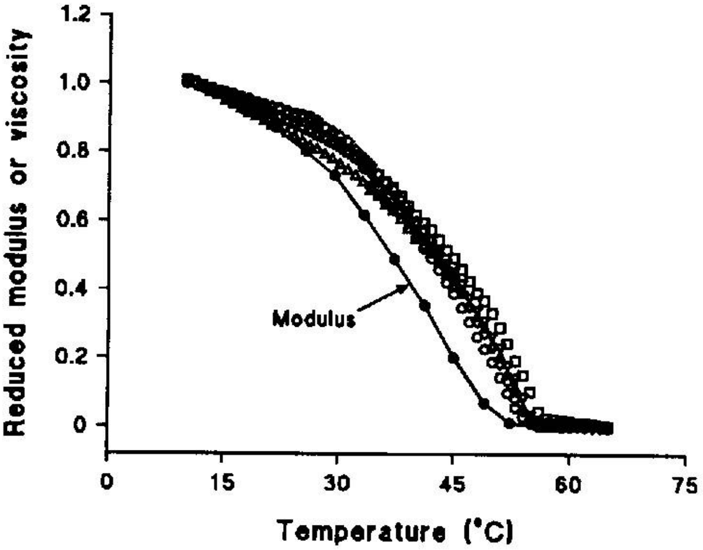

Fig. 2 Water gel: comparison of reduced viscosities for gelation under shear (data from fig. 1) and reduced modulus

Comparing the modulus data with the viscosities, the general shape of the curves is similar, but the viscosities are in general higher. This result is not too surprising, since it is known that the viscosity of a sample passing through the sol-gel transition begins to rise before its elasticity (see for instance ref. 6). This is because the connectivity required for viscosification is less: large aggregates in solution suffice, than for gelation, which requires an aggregate spanning the sample volume. Of course, the data shown in fig. 2 are different from those measured close to a sol-gel transition since the sample is in the gel state at all temperature below 57°C, but prevented from gelling by the applied shear. However, there are parallels between the two situations. They can be summarised by saying that viscosity rise occurs before elasticity rises when a sample passes from sol to gel.

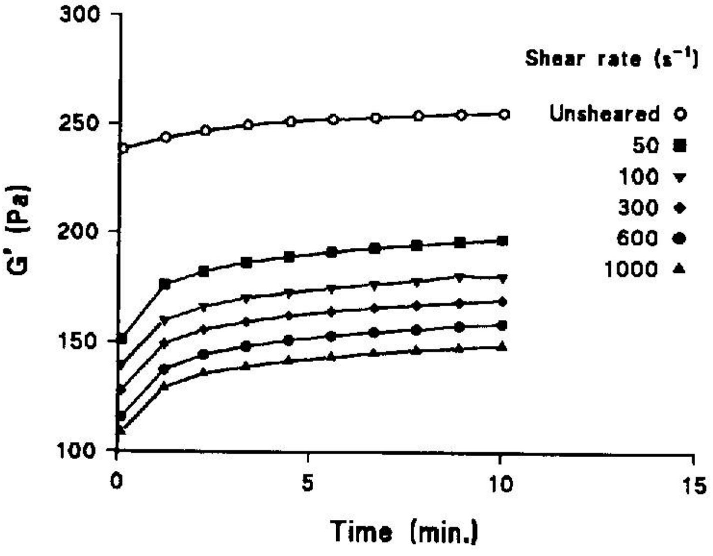

Fig. 3 Water gel: effect of shear rate during gelation on the subsequent recovery

Fig. 3 shows the corresponding recovery curves of the same samples used to obtain the data in fig. 1. The kinetics of recovery apparently vary little with shear rate, but the plateau value attained after 10 min. is reduced by the shear rate during gelation. Thus, ι-carrageenan gels are only partially thixotropic. This result too is surprising. Our intuition was that the thixotropy would be close to complete for all shear rates, but that its kinetics would vary with the imposed shear rate.

Fig. 4 shows the normalised thixotropic recovery as a fraction of the recovery 10 minutes after reaching 10°C. This graph shows that the kinetics of fractional recovery are independent of the shear rate, indeed the agreement between the separate experiments is very satisfying. This master curve cannot be fitted to a single exponential. The initial rise is much too rapid. However it can be reasonably modelled by an instantaneous recovery followed by an exponential relaxation. Thus there seem to be two independent processes at work; the first is extremely fast, causing 75% of the total recovery m the first 10 seconds after shear stops, and the second is much slower forming the rest of the structure in the next 10 minutes (for this concentration of carrageenan). Peigney-Nourry [2] studied the elastic recovery of cold sheared carrageenan gels and found similar kinetics, which were well modelled by a double exponential relaxation. This model would also fit the data in fig. 4. She suggested that the fast component was due to the thixotropic recovery and the slow component to the fact that gelation of the unsheared gel was not complete when shear occurred. The data in fig. 4 contradict this point of view, as the slow component of the sheared gels is much larger than that of an unsheared gel, so we maintain that the recovery has two components.

These results are relevant to understanding the structure of ι-carrageenan gels, which is still unknown [7], although it seems clear that the junction zones are formed by side-to-side interactions between double helices, rather than simply by helix-formation [7], as seems to be the case for gelatin. The former model is in closer accord with the very rapid thixotropic recovery observed here, as it has much fewer topological constraints for cross-linking than the latter.

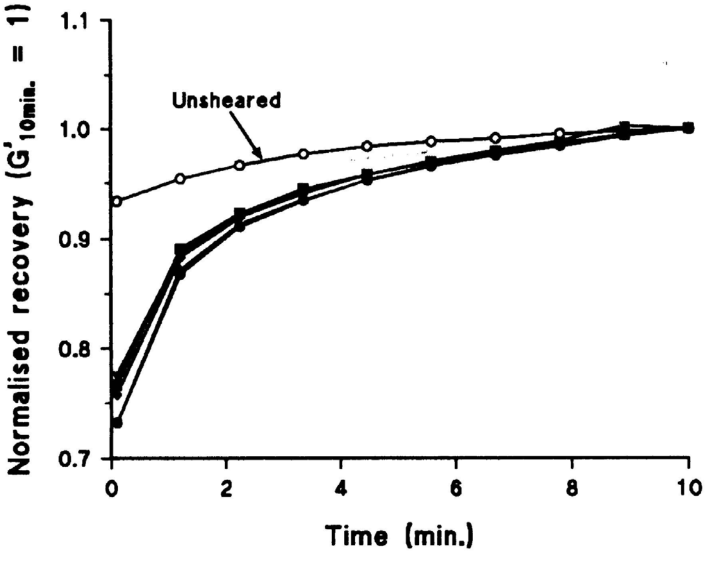

Fig. 4 Water gel: effect of shear rate during gelation on the normalised recovery (same symbols as fig. 3)

Water gel: effect of cold shearing

The gel was gelled under shear at 600s^{-1} under the same conditions as previously, and then sheared for 2 minutes at the same rate, after waiting between 15 minutes and 4 hours at 10°C. Fig. 5 shows the thixotropic recovery as a function of the waiting time before shearing. For this system the waiting time has no effect on either the extent or the kinetics of recovery. As for gelation under shear, the recovery is not total, only about 80% of the modulus of a sample not cold sheared is recovered in 10 minutes.

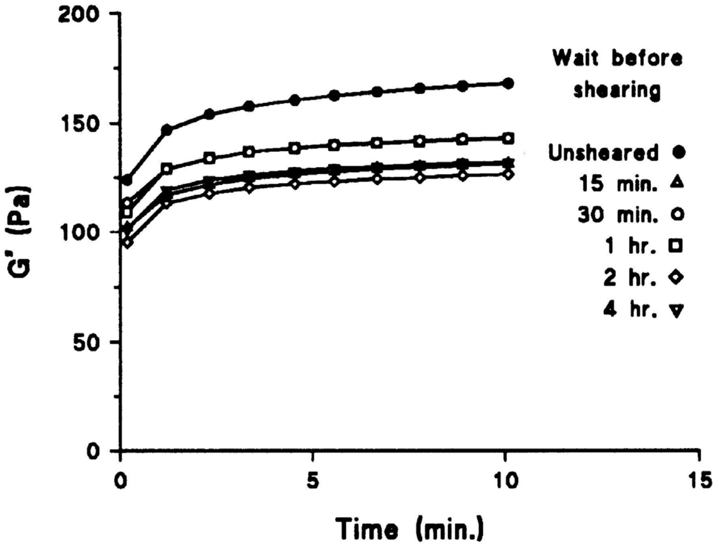

Fig. 5 Water gel: effect of maturation time (after gelation under shear at 600s^{-1}) on recovery after cold shearing

Milk gel: effect of shear during gelation

Figure 6 shows the effect of shear rate during gelation under shear on the subsequent recovery of milk gels. Comparing fig. 6 with fig. 3 (note the different scales of the absiccae), it can oe seen that the extent of recovery after 10 minutes is lower for milk gels, about 20%, as compared with 50 to 75% for the water gels. The fast component of the recovery is also a much smaller fraction of the recovery after 10 minutes for the milk gels: about 30%, as compared with about 80% for water gels. It is also clear that the kinetics of recovery after gelation under shear for milk gels is much slower than for a water gel, whereas the evolution of the unsheared samples is similar: after 10 minutes the shear modulus is constant.

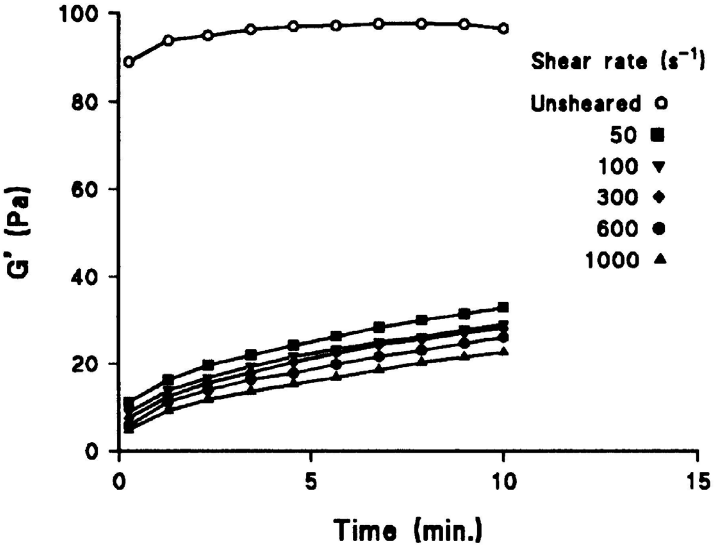

Fig. 6 Milk gel: effect of shear rate during gelation on the subsequent recovery

Again, these data are difficult to interpret, because very little systematic study has been made of the rheology of *unsheared* carrageenan milk gels. The greater loss of structure of milk gels, as compared to water gels, due to gelation under shear implies that the casein-carrageenan links which reinforce the milk gels are much less reversible than the carrageenan-carrageenan links which form the water gel.

Milk gel: effect of cold shearing

Fig. 7 shows the effect of maturation time on the recovery after cold shearing. The conditions are the same as those used for the water gels.

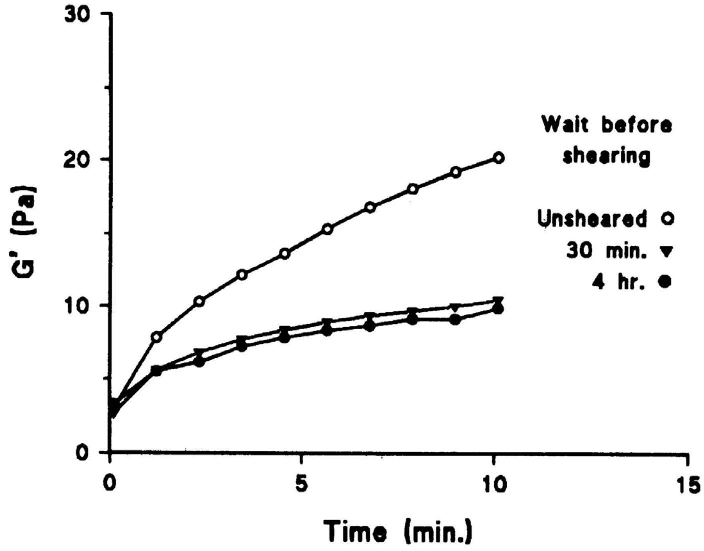

Fig. 7 Milk gel: effect of maturation time (after gelation under shear at 600s^{-1}) on recovery after cold shearing

As for the water gels, see fig. 5, there is no dependence of either the extent or kinetics of recovery on the maturation time. The rapid component of the recovery seems to be unaffected by cold shearing, whereas the slow component is considerably reduced, so that cold shearing leads to a considerable loss of final gel strength, but has little effect on the fast component of the recovery.

Model dessert: effect of shear during gelation

The same dessert had the same carrageenan concentration as the milk gel, but with the addition of modified starch and sugar. First, the sample was prepared on a pilot plant scale, but not passed through the heat exchanger. The effect of shear rate on the gelation under shear was studied in the same way as for the water gels and milk gels, see fig. 3 and 6. Fig. 8 shows the results.

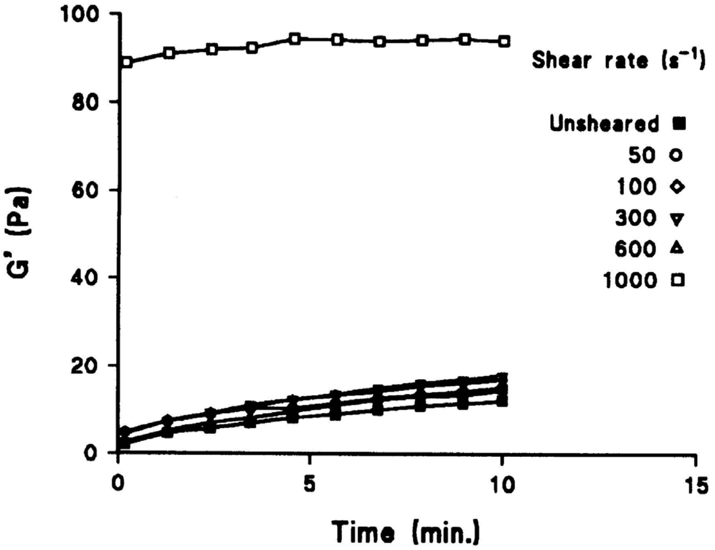

Fig. 8 Model dessert: effect of shear rate during gelation on the subsequent recovery

The recovery is very similar to that of milk gels shown in fig. 6: only 15 to 20% of the gel strength is recovered in 10 minutes, the kinetics of recovery is much slower than in the absence of shear.

Milk dessert: effect of cold shearing in a rheometer

Figure 9 shows that, as for milk and water gels, the effect of maturation time on model desserts is small. Only 10% reduction in recovery occurs between waiting for 30 minutes and waiting for 4 hours. As for the other systems, the fast component is unaffected by the maturation time.

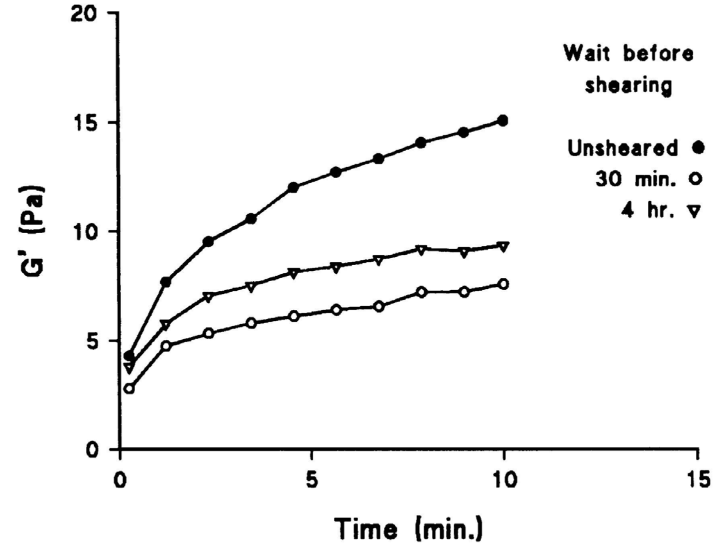

Fig. 9 Model dessert: effect of maturation time (after gelation under shear at 600s^{-1}) on recovery after cold shearing in a rheometer

Comparing fig. 9 with fig. 7, it is surprising that the gel strength of the model dessert is not greater than that of the milk gel The addition of starch to the formulation would certainly be expected to reinforce the gel, but this is not observed in the experiments in the rheometer, although it *is* seen in the measurements made using the pilot plant. We plan to verify this result.

Model dessert: effect of cold shear using the homogenizer

First, the effect of maturation time was measured on the thixotropic recovery of a model dessert, produced using a time/temperature/shear history close to that of a manufacturing plant. The first sample was taken at the outlet of the plate heat exchanger and transferred to the rheometer as rapidly as possible. Measurements began 2 minutes after production. Subsequent samples were cold sheared at various maturation times using a low power laboratory homogeniser to simulate the pumping of the gel from the storage tank into the pot.

Fig. 10 shows the results. They reflect the practical know-how described in the introduction.

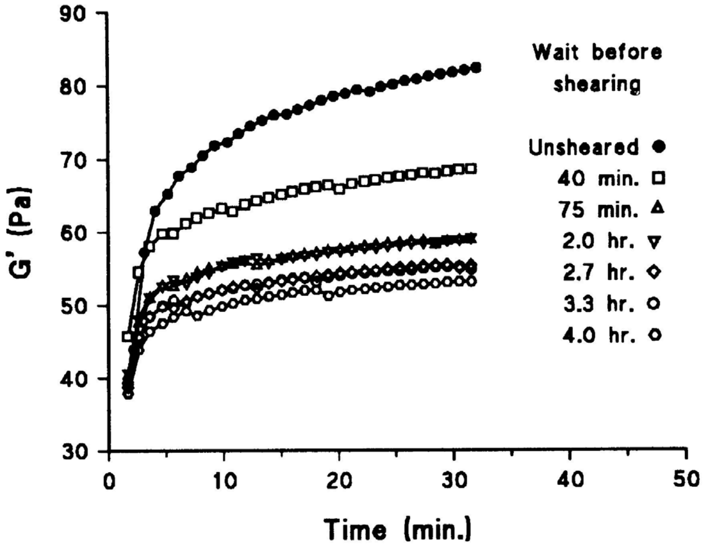

Fig. 10 Model dessert: effect of maturation time (after gelation under shear in a heat exchanger) on recovery after cold shearing, using a homogenizer

Cold shearing soon after gelation causes a loss of thixotropic recovery which increases rapidly with maturation time. On the other hand, the thixotropic recovery is practically independent of maturation time if the latter exceeds two hours. The two stage kinetics of recovery, noted above, is still present in the dessert. It is interesting to note that the rapid component of the recovery hardly depends on maturation time; it is the slow component which disappears after long maturation times.

In the introduction, it was stated that a maturation time is necessary in a traditional manufacturing plant, whilst waiting for a filling line to become available. Economics and logistics dictate that a production line cannot be entirely dedicated to one multi-layer dessert. In fact, the data in fig. 10 suggest a better solution to this problem: the dessert should be stored at a temperature above its gel point, after heat treatment, but before cooling. When a filling line becomes available, the solution is cooled through its gel point in the heat exchanger and immediately pumped into the pot. This arrangement has two advantages: firstly, the dessert rheology is consistent, since the maturation time is always the same, and close to zero; secondly, the loss of thixotropic recovery due to long maturation times is minimised, reducing the formulation costs for a given texture. However, constraints due to plant design often prevent the adoption of this solution.

Conclusions

It has been shown that ι-carrageenan gels are only partially thixotropic under a wide range of conditions. Both the viscosity during gelation under shear and the subsequent elastic recovery scale in a simple way with shear rate, so that master curves can be obtained. The kinetics of thixotropic recovery appears to be in two stages, the majority of the recovery occurs in the 10 seconds after shearing stops. It is this rapid recovery which makes ι-carrageenan a useful product for multi-layer desserts. The thixotropy of milk gels is similar to that of water gels, although the fractional recovery after shearing is less. The effect of gel maturation time before cold shearing observed for dairy desserts is not intrinsic to ι-carrageenan gels, but is a characteristic of the dessert formulation.

References

1. Elliot, J. H. and Ganz; AJ. *J. Food Sci.* **40**, 394 (1975).
2. Peigney-Nourry C. thesis, ENSIA, Massy, France (1987).
3. Mewis, J. *J. Non-Newtonian Fluid Mech.* **6**, 1. (1979).
4. Mewis, J. and De Bleyser, R. *J. Coll. Inter. Sci.* **40**, 360 (1972).
5. Parker, A.; Brigand, G., .Miniou, C., Trespoey, A. and Vallée, P. *Carbohydr. Polym.* **20,** 253 (1993).
6. Axelos, M.A. and Kolb, M. *Phys. Rev. Lett.* **64**, 1457 (1990).
7. Picullel, L. *Food Sci. Technol.* **160**, 239 (2006).

Chapter 8

Discussion and Conclusions

Summary

In chapter 2 ("How does xanthan stabilise salad dressing?"), we studied the creaming behaviour of model pourable salad dressings over a wide range of xanthan and oil phase concentrations. They were produced by mixing a colloidally stable emulsion with xanthan solutions. The model dressings were completely flocculated by depletion at all xanthan concentrations >0.1 g/L. Creaming behaviour was in three phases: an initial delay phase, followed by more or less linear creaming and finally cream compression. Delayed creaming has not been reported previously. It is of great practical interest, because a complete absence of creaming is the aim of successful dressing formulation. The length of the delay phase was proportional to the emulsion concentration, inversely proportional to the oil/aqueous phase density difference and scaled over more than four orders of magnitude with the xanthan concentration to powers between 3 and 4. Traditionally, the stabilisation of salad dressing by xanthan is explained by the yield stress of its solutions. It is shown that they do not have one, and we offer an alternative explanation. It is suggested that the depletion flocculation of the emulsion droplets, induced by the addition of xanthan, leads to the formation of a particle network and that it is the time-dependent yield stress of this network which stabilises the dressing.

Chapter 3, ("Delayed sedimentation as a paradigm for formulating gravitationally stable dispersion") reviews progress in understanding the effects of gravity on colloid/polymer mixtures. There are no scientifically well-founded tests to predict the shelf life of colloidal dispersions. Here "shelf life" means "time without visible effects of gravitational instability". Prediction is difficult because visible sedimentation is often neither immediate nor absent. It starts suddenly after a delay that may be several months. Delayed sedimentation occurs in a wide range of weakly flocculated colloidal dispersions. These systems are temporarily trapped (jammed) far from equilibrium. When jamming is too weak the system sediments immediately. When jamming is too strong, then the system "never" sediments. Jamming is favoured by: high volume fraction, strong flocculation and low gravitational stress. The phenomenology of delayed sedimentation is reviewed, concentrating on emulsions depletion-flocculated by polymer. New data for scaling of the delay time with polymer volume fraction and gravitational stress are discussed. There is no theory yet to predict the delay time. Possible elements of a theory are discussed.

In chapter 4 ("Elasticity Due to Semiflexible Protein Assemblies near the Critical Gel Concentration and Beyond"), we concluded that the elasticity of gelatin gels over a large range of gelatin concentrations can be described by a single model. It assumes that the elasticity is due to contacts between the rods formed by the helices. The model combines a percolation model for low helix concentrations with a model based on the deflection length for high helix concentrations. It improves on previous models for the gel strength of gelatin gels over its entire concentration range. It should be equally applicable to other semi-flexible rod systems over a large concentration range.

In chapter 5 (“Scaling in the dynamics of gelatin gels”), we studied the gelation kinetics of gelatin gels. We concluded that they never reach equilibrium. The storage modulus increases linearly in log(time) after some initial time, typically one hour. This behaviour, which is characteristic of physical aging, makes it hard to define the gelation concentration, gelation temperature and gel melting temperature in a non-arbitrary way. For instance, after slight heating close to the gelation temperature certain gels melt, but then reform several hours later. The gelation kinetics for all temperatures, concentrations, molecular weight distributions and times can be parameterised by forming master curves in log(elasticity)/log(time) space. The effects of temperature and concentration are independent. For concentrations between 7.5 and 100 g/kg we find no evidence for a critical gelation concentration. For a given sample, all the data can be fit using a single critical temperature, which shows the characteristics of the critical temperature of a second order phase transition. There are two regimes with different critical exponents. We call these “close-to-critical” and “far-from-critical”. Cuts made in a gel during the close-to-critical regime heal, whereas cuts made once a gel is in the far-from-critical regime do not heal. The effects of temperature jumps in the two regimes are qualitatively different. Both show scaling properties. These results are discussed in the context of the physics of out of equilibrium systems.

In chapter 6 (“Spin glass-like dynamics of gelatin gels”), we show the analogies between the behavior of gelatin gels and spin glasses. In particular, we reproduce the memory and rejuvenation effects observed by Jonasen et al. [1]. We suggest that gelatin gels are “colloidal spin glasses”. Their transparency and convenient length and time scales means that the microscopic dynamics can be studied directly, unlike spin glasses.

In chapter 7 (“Thixotropic carrageenan gels and dairy desserts”), we studied the rapid thixotropic recovery of gels of iota carrageenan that is a key factor in their use in the production of multi-layer dairy desserts. The thixotropy of both water gels and model dairy desserts has been studied. The results of thixotropic recovery in a rheometer after: i) gelation under shear and ii) subsequent cold shearing are compared for aqueous gels, milk gels and model dairy desserts. These measurements are compared with the recovery of samples sheared during processing on a pilot plant. Thixotropic recovery was never complete and appeared to be divided into a fast and a slow component. Both the viscosity during gelation under shear and the kinetics of recovery can be scaled, so that results for all shear rates form a single master-curve. For cold shearing of already formed gels the maturation time before shearing was not a significant factor for aqueous or milk gels, but caused significant differences in the final texture of model dairy desserts treated on a pilot plant.

Suggestions for future studies

I hope that the work described here will encourage physicists to apply their methods to the systems I have studied. There is still plenty left to do.

Polymer-thickened emulsions

This system has attracted a lot of interest since the study described in chapter 2, partly due to its intrinsic interest for physicists and partly due to the generality of the “shelf life problem” in the formulation of complex fluids. In particular, David Weitz’ group at Harvard has made several significant advances [2-4].

- It would be interesting to know whether these systems, or at least some of them, show intermittent dynamics. The latest camera-based systems for making light scattering measurements should give a clear answer to this question [5]. Another apparatus that should be tested is the commercial system “Horus”, developed by Cipelletti et al. [5] and sold by “Formulaction” to study drying films. The results might provide the basis of a predictive test.
- We still lack a predictive test for the shelf life of complex fluids. The scaling with gravitational stress shown in chapter 2 should be explored further.

Gelatin gels

- Gelatin gels are also predicted to show intermittency. This observation will confirm the applicability of Sibani’s elegant picture of the origin of aging and spin glass dynamics [6].
- The complex dynamics described in chapter 5 still require a lot of work to understand fully. We have shown some interesting scaling, but the results are purely phenomenological.
- A remarkable observation made in chapter 5 deserves pursuing: when young gelatin gels were cut and then placed back together, the cut healed, whereas the cuts in older gels did not heal. This theme of two regimes in the growth of gels also appears from time to time in other references. For instance Gornall and Terentjev [7] showed that helix growth occurred for some time before aging starts.
- I think that it is highly probable that other thermoreversible gels will also show spin glass dynamics. Obvious candidates are: iota carrageenan, kappa carrageenan and high methoxy pectin gels (i.e. fruit jam).
- The model described in chapter 4, which relates helix concentration to elasticity, should be applicable to other gels formed from helices; in particular all the gels cited in the previous paragraph.
- Much of the work on experimental spin glasses is concerned with the effects of magnetic fields, sometimes in combination with those of temperature. The closest analogy in gelatin gels is the effect of stress. It would be very interesting to pursue this idea. The additional effects of nonlinear viscoelasticity will add more complexity.

Iota carrageenan gels

- these fascinating gels have hardly been studied since the work described in this thesis. For instance, we still lack basic data connecting the helix fraction with the elasticity. The models developed here for gelatin gels may be relevant. However, no model for the remarkable, almost instant, mechanical reversibility is in sight.
- Baravian et al [8] showed that the fast gelling of ι-carrageenan gels could be prevented if they were sheared *for 16 hours*. As Lennart Piculell remarked to me at the time: “where does this huge timescale come from?” Now we are better placed to answer: it must be related to aging. This phenomenon certainly deserves study

Conclusions

The jamming picture provides a powerful way of making parallels between extremely diverse out-of-equilibrium systems, including those studied here. Much of the behavior does not depend on the detailed features their microscopic components: it is dominated by the generic features of the jammed state.

The black and white picture (either permanently jammed or permanently unjammed) of the jamming paradigm is too simple. Jammed systems are metastable, so they can, and do, evolve.

Physical aging is a generic feature in the time-dependence of jammed systems.

The connection between spin glasses and gels brings a powerful new set of tools to understand the out-of-equilibrium dynamics of jammed systems.

Understanding the generic features of jammed systems can transform what has been empirical knowledge, full of arbitrariness and surprises, into rational, durable, scientific expectations.

References

1. K. Jonason et al., Phys. Rev. Lett., **81**, 3243 (1998).
2. M. L. Kilfoil, E. E. Pashkovski, J. A. Masters, and D. A. Weitz, Phil. Trans., **361**, 753 (2003).
3. C. Kim et al., Phys. Rev. Lett., **99**, 028303-028303/4 (2007).
4. S. Manley, J. M. Skotheim, L. Mahadevan, and D. A. Weitz, Phys. Rev. Lett. **94**, 218302-218302/4 (2005).
5. L. Cipelletti et al., J. Phys: Condensed matter, **15**, S257-S262 (2003).
6. P. Sibani and H. J. Jensen, Europhys. Lett. **69**, 563 (2005).
7. J. L. Gornall and E. M. Terentjev, Phys. Rev. E, **77**, 031908-031908/8 (2008).
8. C. Baravian, D. Quemada, and A. Parker, J. Texture Studies, **27**, 371 (1996).

Acknowledgements

I have many people to thank for their help during this extended work.

The key component of any PhD is the supervisor. Erik van der Linden has been a fine guide and coach for an unusual PhD student. Without his encouragement and help, I would never have arrived at my goal. I have a great admiration for his exceptional combination of scientific and management skills. His suggestion that “Self Organized Criticality” (SOC) was relevant to chapters 5 and 6 was key, even if it is not mentioned elsewhere in the final text. It was a vital stepping stone to reach Paolo Sibani’s ideas connecting SOC and aging.

Several fine technicians carried out part of the experimental work. First to mention must be Florence Vigouroux, who made beautiful measurements that contributed to chapters 2 and 3. I salute her capacity to transform my sometimes vague instructions into reproducible results. Patrick Vallée did the nice systematic measurements on iota carrageenan shown in chapter 7, during my time with SBI in Normandy. Christian Miniou made some of the measurements in chapter 3. With his experience, fine eye and patience, he taught me a lot about food polysaccharides.

The initial work on creaming kinetics was carried out at IFR Norwich by Margaret Robbins’ group. I well remember the day that she rang to announce the observation, by Kim Ng, of the strange creaming kinetics that became delayed sedimentation. It was an authentic “Eureka” moment.

The work on gelatin was a memorable extended collaboration with Valéry Normand, one of the best experimentalists that I have ever met. We had a great time trying to work out together the complex phenomenology described in chapter 5.

The spin glass work would have been impossible without the generous advice and help of several experts. Jorge Kurchan kindly got us going in the right direction. Sergio Ciliberto gave us excellent advice, especially the key idea that we should apply the cool & heat cycle used by Nordblad et al. to study spin glasses. His wonderful experimental work has been an inspiration ever since. Eric Vincent, one of the world’s leading spin glass experimentalists, was extremely kind. He gently corrected many beginner’s mistakes and generously invited Valéry Normand and I to Saclay to present our results. Paolo Sibani has helped immensely. The day that I typed “SOC” and “aging” into Google was a turning point in this work. His was almost the only name that appeared. I believe that his clear vision of the origins of aging provides the only credible generic picture for understanding why spin glasses and gelatin gels behave similarly.

I would like to mention the French physicist Catherine Allain, who sadly died in 2006. Her work on sedimentation was an inspiration. I feel that her work deserves greater recognition. I still have copies of the letters that we exchanged.

I must acknowledge my huge debt to two great scientists and friends: Daniel Quemada and Christophe Baravian. I feel that they both deserve much greater recognition than they receive; no doubt because they are both admirably modest and not inclined to “market” themselves. Without their help, I would not dare to call myself a rheologist. However, they are both much more. Over the last 15 years, I have also discussed with them all manner of subjects, including the philosophy and history of science.

I must thank Tony Blake, my first boss at Firmenich, who encouraged me to pursue thoroughly uncommercial research, like the spin glass/gelatin connection. He also actively encouraged me to do this thesis. Our freewheeling scientific discussions were both great fun and useful, making interesting connections that have never been made before. Our foray into cognition, neuroscience and computing was particularly memorable, as neither of us had any qualification to talk about any of those subjects. One of my propositions results from those discussions.

Last and most I must thank my wife, Marie-Noëlle, who has encouraged me and tolerated with immense patience and good humour the time that writing a thesis takes out of family life.

Curriculum vitae

Alan Parker was born on the 3rd of April 1955 in Glastonbury, Somerset, United Kingdom. In 1973 he completed A levels in Chemistry (A), Mathematics (B) and Physics (B) at King's School, Macclesfield, Cheshire, UK. He obtained a BSc in Chemistry (Upper 2nd class) from the University of Bristol in 1976. In 1977 he was awarded an MSc in Surface and Colloid Science by the University of Bristol.

In a long and varied career, he has worked for, among others: the UK Atomic Energy Authority; Dowell-Schlumberger; Malvern Instruments and Sanofi-Bio Industries. Since 1998, he has worked for Firmenich SA in their Corporate Research Division, Geneva, Switzerland.

In 2000 he was elected Fellow of the Royal Society of Chemistry.

He has more than 30 published papers in journals including: Society of Petroleum Engineers Journal, Chemical Senses, Carbohydrate Research, Optics Express, Journal of Texture Studies and the American Institute of Chemical Engineers' Journal. He holds 3 patents.

He has been married to Marie-Noëlle (né Guillot) since 1987. They have 2 children: Thomas (born 1991) and Auriane (born 1994).

List of publications

Refereed journals

"Fast optical sizing without dilution" A. Parker, C. Baravian, F. Caton, J. Dillet, J. Mougel, *Food Hydrocolloids*, **21**, 831 (2007).

"Interfacial Rheology of Surface-Active Biopolymers: Acacia senegal Gum versus Hydrophobically Modifed Starch", P. Erni, E. J. Windhab, R. Gunde, M. Graber, B. Pfister, A. Parker, and P. Fischer, *Biomacromolecules*, **8**, 3458 (2007).

"Size determination by use of two-dimensional Mueller matrices backscattered by optically thick random media" J. Dillet, C. Baravian, F. Caton, and A. Parker, *Applied Optics*, **45**, 4669 (2006).

"Using vane geometry for measuring the texture of stirred yogurt", F. Martin, A., Parker, J. Hort, T. Hollowood, A. J. Taylor, *J. Texture Studies*, **36**, 421 (2005).

"Modeling the Kinetics of Flavour Release during Drinking", V. Normand, S. Avison and A. Parker, *Chem. Senses*, **29**, 235 (2004).

"Gel transition of depletion flocculated emulsions" C.L.A. Berli, D. Quemada and A. Parker, *Coll. Surf. A*, **215**, 201 (2003).

"Vane rheometry with a large, finite gap" C. Baravian, A. Lalante and A. Parker, *Appl. Rheol.* **12**, 81 (2002).

"Modelling the rheology of depletion flocculated dispersions" C.L. Berli, D. Quemada and A. Parker, *Coll. Surf. A*, **203**, 11 (2002).

"Dissolution kinetics of polymer powders" A. Parker, F. Vigouroux and W.F. Reed, *A.I.Ch.E.J.*, **46**, 1290 (2000).

"Gelation kinetics of gelatin: a master curve and network modelling" V. Normand, S. Muller, J.C. Ravey and A. Parker, *Macromolecules*, **33**, 1063 (2000).

"Effect of carrageenan type on the behavior of carrageenan/milk mixtures" V. Langendorff, G. Cuvelier, B. Launay, C. Michon, A. Parker and C.G. de Kruif, *Food Hydrocoll.*, **14**, 273 (2000).

"A novel method for determining the dissolution kinetics of hydrocolloid powders" T.P. Kravtchenko, J. Renoir, A. Parker, G. Brigand, *Food Hydrocolloids* **13**, 219 (1999).

"Light scattering and viscoelasticity of aggregating and gelling κ-carrageenan" V. Meunier, T. Nicolai, D. Durand and A. Parker, *Macromolecules*, **32**, 2610 (1999).

"Casein micelle/carrageenan interactions in milk: influence of temperature" V. Langendorff, G. Cuvelier, B. Launay, C. Michon, A. Parker and C.G. de Kruif, *Food Hydrocolloids*, **13**, 211 (1999).

"Gelation and flocculation of casein micelle/carrageenan mixtures" V. Langendorff, G. Cuvelier, B. Launay and A. Parker, *Food Hydrocolloids*, **11**, 35 (1997).

"Phase behavior of gelatin/oligosaccharide mixtures" C. Vinches, A. Parker and W. Reed, *Biopolymers*, **41**, 607 (1997).

"Modelling thixotropy using a novel structural kinetics approach: basis and application to a solution of iota carrageenan" C. Baravian, D. Quemada and A. Parker, *Journal of Texture Studies*, **27**, 371, (1996).

“Viscoelastic properties of ι-carrageenan/gelatin mixtures” C. Michon, G. Cuvelier, B. Launay and A. Parker, *Carbohydrate Polymers*, **331**, 161 (1996).
“Binding of galactomannans to kappa carrageenan after cold mixing”, A. Parker, D.Lelimousin, C. Miniou, and P. Boulenguer, *Carbohydrate Research,* **272**, 91 (1995).
“How does xanthan stabilise salad dressing?”, A. Parker, P. Gunning, K. Ng and M. Robins, *Food Hydrocolloids*, **9**, 333 (1995).
“Rheology and fracture of mixed ι- and κ- carrageenan gels: Two step gelation”. A. Parker, G. Brigand, C. Miniou, A. Trespoey, and P. Vallée, *Carbohydrate Polymers* **21**, 253 (1993).
“Using elasticity/temperature relationships to characterise gelling carrageenans” A. Parker, *Hydrobiologia*, **260/261**, 583 (1993).
“Advances in zeta potential and size measurement of colloidal particles” A. Parker and P. McFadyen, Am. Lab. **22**, 34 (1990).
“Experimental and theoretical study of polymer flow in porous media” K.S. Sorbie, A. Parker and P.J. Clifford, Society of Petroleum Engineers Journal, Aug. 1986, 281 (1986).
“A flow ultramicroscope for particle counting and size distribution analysis” D.J. Walsh, J. Anderson, A. Parker, M.J. Dix, Coll. Polym. Sci., 259, 1003-9 1981.

Conference proceedings

“Scaling in the dynamics of gelatin gels” V. Normand and A. Parker, *Proc. 3rd Int. Symp. Food Rheol. Structure*, eds. P. Fischer, I. Marti and E.J. Windhab, 185-192, 2003.
“Texture Profiling with the Vane: a general method for characterizing the texture of soft food” A. Parker and F. Vigouroux, *Proc. 3rd Int. Symp. Food Rheol. Structure*, eds. P. Fischer, I. Marti and E.J. Windhab, 131-136, 2003.
“A gas-liquid interfacial mass-transfer cell for studying flavor release” A. Parker and M. Marin in “Flavor Release”, eds. D.D. Roberts and A.J. Taylor, *ACS Symp. Ser.* 763, 192-200, 2000.
“Effect of the addition of high methoxy pectin on the rheology and colloidal stability of acid milk drinks”. A. Parker, P. Boulenguer and T.P. Kravtchenko in *“Food Hydrocolloids: Structures, Properties and Functions”*307-312, edited by K. Nishinari and E. Doi, published by Plenum Press, 1994.
“Rheology of mixed carrageenan gels: opposing effects of potassium and iodide ions”, A. Parker* in *“Food macromolecules and colloids”*, edited by E. Dickinson and D. Lorient, published by the Royal Society of Chemistry, 1995.
“Colloidal stability and sedimentation of pectin-stabilised acid milk drinks”, T.P. Kravtchenko, A. Parker and A. Trespoey in *“Food macromolecules and colloids”*, eds. E. Dickinson and D. Lorient, 1994.
“Thixotropic carrageenan gels and dairy desserts”, A. Parker and G. Tilly, *Gums and Stabilisers in the Food Industry*, 7, 393-401, 1994.