

Gelation Temperature of a Gelatin Solution Determined by Diffusing Wave Spectroscopy

Introduction

Diffusing Wave Spectroscopy (DWS) is a modern light scattering technique that is mainly utilized to probe the motion of particles in colloidal media [1]. A microrheological analysis of the particle motion may further provide the medium's rheological properties, namely the frequency-dependent storage and loss moduli, $G'(\omega)$ and $G''(\omega)$, respectively [2]. DWS can be applied to a rich variety of soft-matter systems, including gelling systems. In particular, DWS is able to accurately characterize their gel point, defined when the normalized intensity correlation function (ICF) no longer decays to zero [3]. Gelatin solutions (Figure 1a) are dispersions of biopolymers in water that form physical gels below the gelation temperature T_{gel} (Figure 1b)[4,5]. Furthermore, at the gelation temperature of polymeric gel-forming liquids, $G' \sim G'' \sim \omega^n$, where $0.19 < n < 0.92$ [6]. In this application note, we propose to determine T_{gel} of a food grade gelatin solution using the DWS RheoLab from LS Instruments.

Sample Preparation

Commercial gelatin was dissolved at 2.5 wt% (weight by weight) in deionized water at $T = 50^\circ\text{C}$. To perform DWS on this transparent mixture, 784 nm diameter tracer polystyrene particles (microParticles GmbH®) were added at a concentration of 1 wt%. At such a particle concentration, the sample appears white (Figure 1). Subsequently, the solution was introduced into a 5 mm thick glass cuvette at 50°C , which was loaded in the DWS RheoLab. Then, the gelatin solution was progressively cooled from 50°C to 15°C , with temperature steps of 5°C down to 30°C , and steps of 0.5°C from 30°C . At each temperature, a waiting time of 30 min was observed before measuring. Cooling rate was shown not to influence the gel point of gelatin [7,8]. The transport mean free path l^* of the sample was determined using the DWS RheoLab; l^* was $290 \mu\text{m}$ over the temperature range studied.

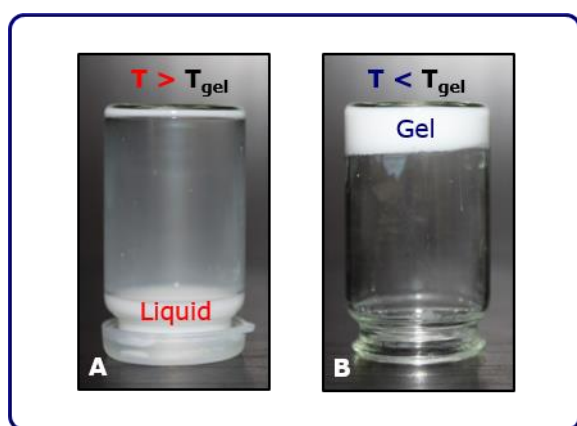


Figure 1. a) liquid and b) gel phases of the gelatin solutions containing 1 wt% of 784 nm diameter polystyrene particles.

Results and Discussion

In the liquid phase above T_{gel} , the ICFs, obtained in transmission, decay to zero, but remain finite in the gel phase below T_{gel} (Figure 2a). As the sample is further cooled in the gel phase, however, the height H of the plateau of the ICF curves at large values of τ is observed to increase (Figure 2). To quantify the latter observation, the normalized ICFs were fitted using the following function: $f(\tau) = A \times \exp(-\tau/\tau_C) + H$, where A and τ_C are the amplitude and the characteristic time of the decay, respectively. According to Schurtenberger et al.[3,] the definition of the gel point is when H rises from zero. **Therefore, $T_{gel} = 22.5^\circ\text{C}$.**

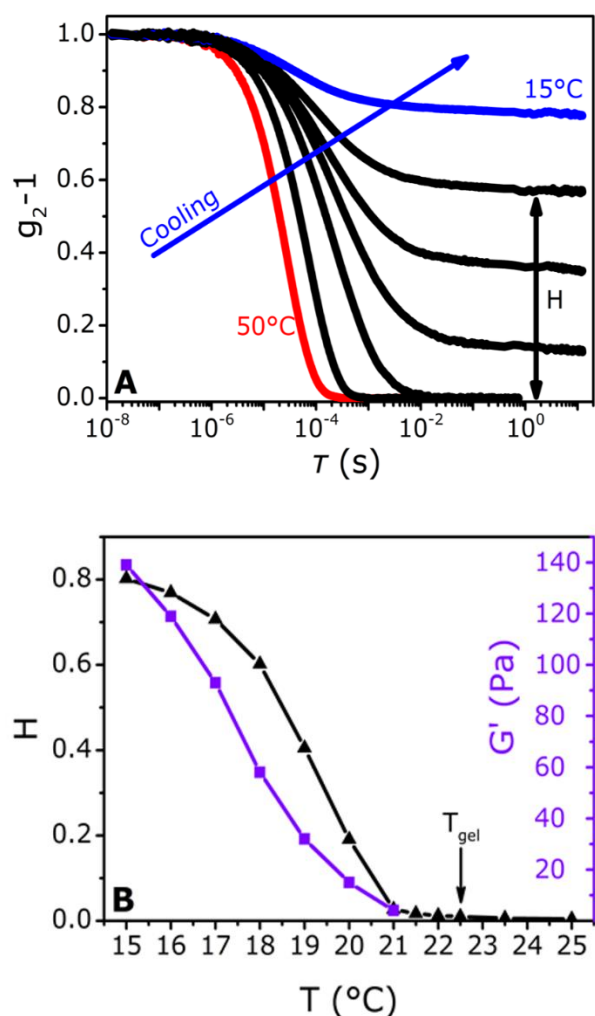


Figure 2. a) ICFs measured when cooling the sample (an arrow indicates the direction of the curve change), b) H and G' ($\omega=100$ rad.s⁻¹) vs. T .

In addition, the increase of H with further decrease of T to 15°C is a consequence of the progressively restricted particle motion. This is due to the strengthening of the forming gel, as shown in Figure 2b, where H follows the same trend as the elastic modulus G' , taken at $\omega = 100$ rad.s⁻¹. After automatically extracting the particle mean square displacement (MSD) from the ICFs (Figure 3a), the *DWS RheoLab* software can accurately compute both $G'(\omega)$ and $G''(\omega)$ upon application of the Generalized Stokes-Einstein Relation (GSER) to the particle MSD (Figure 3b) [2]. In the liquid phase, the MSD and G'' are linear with τ and ω respectively, indicating a purely viscous fluid. In the gel phase, the MSD and G' saturate at long τ and low ω values respectively. This reflects the elastic behavior of the medium. At T_{gel} as

defined above, $MSD \sim \tau^{0.8}$, and the relation $G' \sim G'' \sim \omega^n$ with $n = 0.8$ is verified. Moreover, the magnitude of n is consistent with values previously obtained for similar systems [4,5]

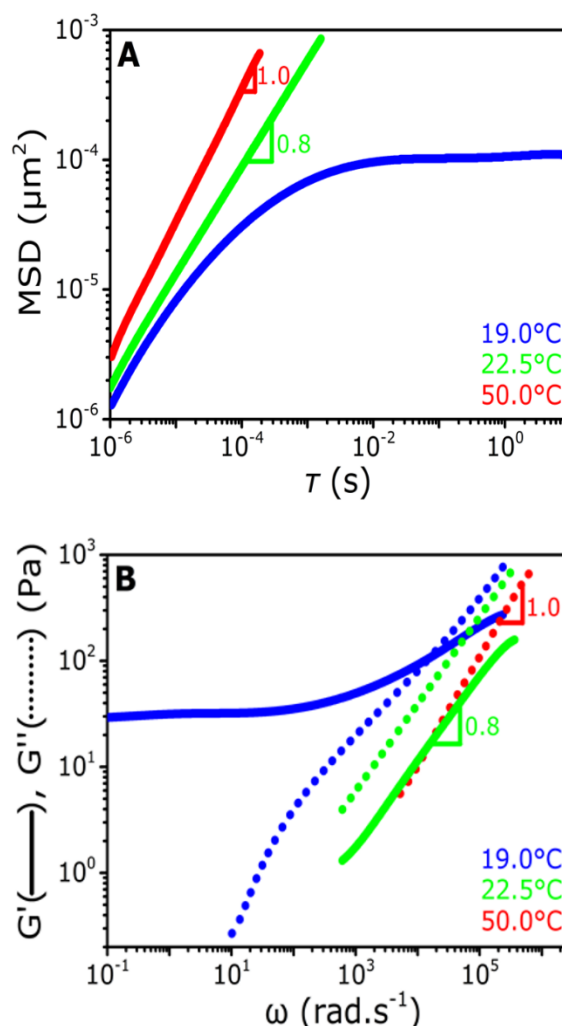


Figure 3. a) MSDs, b) Microrheology curves computed by the *DWS RheoLab* software from the MSDs using the GSER.

Conclusion

Using the *DWS RheoLab*, we have successfully and unambiguously determined the gelation temperature T_{gel} of a commercial, food grade gelatin solution as $T_{gel} = 22.5^\circ\text{C}$. Aging of gelatin gels could be further studied using the *DWS RheoLab* since it facilitates time-dependent measurements.

References

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