A RHEO-OPTICAL INVESTIGATION INTO THE VISCOELASTIC MODULI OF ACIDIFIED MILK GEL

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Abstract

Diffusing wave spectroscopy (DWS) in the backscattering geometry was employed to observe the evolution of the intensity correlation function during the acidification of skimmed milk by gluconic-δ-lactone (GDL). At the stage when the formation of casein particle gel is largely complete the correlation function at shorter decay times reveals the local structural arrest of the casein micelles, whereas at longer delay times it illustrates the hindered slow motion of casein micelle aggregates. We use the principles of the approach suggested by Mason, Gang and Weitz, linking the optically measured mean square displacement, $\langle \Delta r^2(t) \rangle$, of the microscopic particles in a dense colloid to its viscoelastic properties, to provide an estimate of the frequency dependent viscoelastic modulus of the acidified milk gel (AMG). We compare the viscoelastic moduli measured by the conventional mechanical rheometry with the optically measured ones. The results of the two different experimental methods are found to be in reasonable agreement.

Kurzfassung

Diffusionswellenspektroskopie (DWS) in der Rückstreuungsgeometrie wurde für die Entwicklung der Intensitätskorrelationsfunktion von gluconischer δ-Lactene (GDL) entrahmter Milch eingesetzt. Auf der Stufe der größtenteils abgeschlossenen Ausbildung der Kasein-Gelpartikeln zeigt die Korrelationsfunktion kürzere Zerfallszeiten an, die auf die lokale strukturelle Behinderung der Kasein-Myzellen hinweisen, während die längeren Zerfallszeiten aus der behinderten, schleichenden Bewegung der Kasein-Myzellaggregaten resultieren. Wir haben das Annäherungsprinzip nach Mason, Gang and Weitz angewendet, bei dem der auf optischem Weg gemessene mittlere quadratische Verschiebung $\langle \Delta r^2(t) \rangle$ der mikroskopischen Teilchen in einem dichten Kolloid mit dessen viskoelastischen Eigenschaften verknüpft wird, um eine Abschätzung der viskoelastischen Modulen des angesäuerten Milchgels (AMG) zu ermöglichen. Wir vergleichen die viskoelastischen Module, gemessen mittels konventioneller mechanischer Rheometrie, mit denen auf optischem Weg gemessenen Modulen. Die Ergebnisse der beiden unterschiedlichen experimentellen Methoden ergeben eine annehmbare Übereinstimmung.

Résumé

La spectroscopie d'ondes diffusantes en géomètrie de reflexion a été utilisée pour observer l'évolution de l'intensité de la fonction de corrélation pendant l'acidification de la crème de lait par la lactone-δ-gluconique (GDL). Lorsque la formation de la particule de gel de caséine est bien achevée, la fonction de corrélation révèle, aux temps courts, la structure locale des micelles de caséine, tandis qu'aux temps plus longs, elle décrit le mouvement ralenti des agrégats de micelles de caséine. La méthode suggérée par Mason, Gang et Weitz, permettant de relier les mesures optiques du déplacement carré moyen $\langle \Delta r^2(t) \rangle$ des particules macroscopiques se mouvant dans un colloïde dense aux propriétés viscoélastiques, est utilisée. Elle permet de fournir une estimation de la dépendance fréquentielle du module viscoélastique du gel de lait acidifié (AMG). Nous comparons les modules viscoélastiques mesurés par la rhéomètrie mécanique conventionnelle avec les modules mesurés optiquement. Les résultats obtenus par les deux méthodes expérimentales concordent.

Key words: Diffusing wave spectroscopy, Viscoelastic moduli, Acidified milk gel, Particle gel, Rheometry

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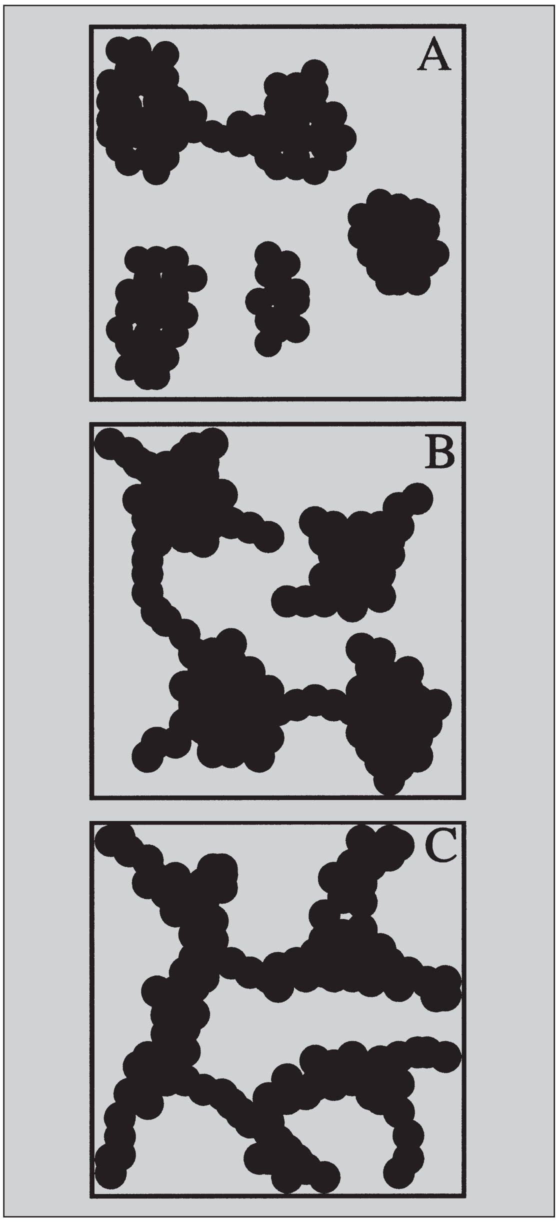
Figure 6: A schematic illustration of the possible structures of the AMG: lumps (A), interconnected lumps (B), and strands (C).



anisms of aggregation, which in turn depend on the interplay of the interparticle potentials and the rates of diffusion [33].

In identifying the entities which contribute to the DWS spectrum in the present study it is important to consider not only the size but also the structure of the aggregates. The possible structures are illustrated in Fig. 6. This schematic drawing, supported by the evidence from the electron microscopy [16] is presented merely to assist visualization. In a gel generated by the addition of GDL to fresh skimmed milk at low temperatures, slow aggregation, produces a 'lumpy' type of aggregate which is nearly spherical in shape with a relatively narrow size distribution [16] loosely inter-connected by thin 'strands' (Fig. 6.b). We treat these quasi-spherical aggregates as the scatterers in the present case. We assume that scattering from the thinner interconnecting strands is insignificant compared to that from the 'lumpy' aggregates. Such assumptions can only produce reasonable results for the 'lumpy' type of cluster, such as shown in Fig. 6.a. Presumably, the stronger the tendency of the gel to be of the 'strandy' type (Fig. 6.c) the more elastic its network would be and the question of the nature of the scattering probe would arise. Therefore, for the gel structure shaped more like a network of thin strands the straightforward approach to the calculation of the modulus based on the use of intrinsic probes-'lumps' as scatterers and the calculations using the equation based on the viscous approximation would not be justified.

In gels, where the 'strands' dominate the picture and the elasticity is considerably higher, the approach would have to be modified to accommodate the effect of a contribution of the dynamics of those interconnecting strands to the elasticity of the gel. To be able to understand the relationship between the optically measures dynamics and the viscoelasticity of real fractal aggregate particle gels we should be taking into account the structure (or shape) of the clusters. An adequate mathematical model is required to accommodate the contributions to the DWS spectrum from the 'elasticity' and the 'viscosity' in dense ($\phi > 0.1$) particle gels.

4 CONCLUSIONS

We have confirmed the possibility of application of DWS to monitor gelation in acidified milk gels and extended the DWS data to the stage of acidification, where the gel formation is largely completed. The 'lumpy' aggregates of the casein micelles loosely interconnected by the elastic 'strands' formed in gluconic-δ-lactone (GDL) induced gel act as scattering elements. Non-invasive, backscattering DWS can be used to probe the relationship between the internal dynamics and the viscoelasticity in the acidified milk gel.

It is shown that, in a particular case of the AMGs prepared from fresh skimmed milk by slow acidification, it is possible to apply the Stokes-Einstein equation to obtain the viscoelastic modulus. We have calculated the mean square displacement of the particles in these gels and used it to calculate the viscoelastic modulus in gels of different strength achieved by varying starting concentrations of the acid precursor GDL between 1.8 and 2.2%. We found a reasonable agreement between the viscoelastic moduli obtained from the mechanical rheometric measurements and the modulus obtained by the calculations from the optical data.

Strong evidence was provided in support of the approach linking the optically probed internal dynamics in dense particle gels to the their viscoelastic properties. For more precision of the quantitative *rheo-optical* analysis measures further investigations of the relashionships between the structure and rheology of the dense particle gels are required.

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