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New trends in optical microrheology of complex fluids and gels

Abstract We have studied various complex systems from particle and biopolymer gels to concentrated surfactant solutions using classical rheometry and optical microrheology. Optical microrheology uses dynamic light scattering, usually in the multiple scattering regime, to obtain information about the microscopic dynamic properties of complex media. This can be done either by direct investigation or by addition of tracer particles to otherwise transparent systems. Based on the local dynamics the macroscopic viscoelastic properties are predicted. We have implemented several new approaches to extend the range of application for optical microrheology: Taking advantage of the recently developed “two-cell technique” we will show how dynamic multiple light scattering (Diffusing Wave Spectroscopy) can be used to investigate the properties of fluid and

solid-like media. Furthermore we have significantly extended the range of accessible correlation times to 10^{-8} – 10^4 s using a CCD based multispeckle analysis scheme. Our experiments cover such different materials as polystyrene latex dispersions and gels, ceramic green bodies, casein micellar gels (yogurt) and giant micelle solutions. Excellent quantitative agreement is found when comparing the results obtained from DWS to classical rheological measurements. However, compared to classical rheology, we were able to significantly increase the range of accessible frequencies using optical microrheology, thereby opening up a wealth of new possibilities for the study of these fascinating materials.

Keywords Microrheology · Diffusing wave spectroscopy · Colloids · Biopolymers · Micelles

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Introduction

In recent years significant progress has been made in the development of modern optical techniques to study and characterise the rheological properties of complex fluids [1–9]. While these techniques have been mostly restricted to fundamental research they now become increasingly available to both industrial and applied researchers [6–11].

The underlying idea of optical microrheology is to study the thermal response of small (colloidal) particles

embedded in the system under study. In this case the particle can either be artificially introduced, which is then called “tracer-microrheology”, or can be part of the system itself, e.g., like in the case of ceramic green bodies. By analysing the thermal motion of the particle it is possible to obtain quantitative information about the loss and storage moduli, $G'(\omega)$ and $G''(\omega)$ over an extended range of frequencies [1–3].

One of the most popular techniques to study the thermal motion of the particles is diffusing wave spectroscopy (DWS) which is an extension of standard

photon correlation spectroscopy (PCS) to turbid media. Here the analysis of (multiply) scattered laser light is used to determine the time evolution of the probe particles mean square displacement [12–14]. DWS allows access to a broad range of time scales which results in the above mentioned large frequency range covered by DWS-based optical microrheology.

The aim of this article is twofold. First we want to show how modern optical techniques can extend and improve classical rheology both in the sense of frequency range and applicability. In particular we will introduce two novel approaches to extend standard optical microrheology, normally restricted to liquid samples, to viscoelastic solids [6, 7, 11]. Secondly we discuss the application of optical microrheology to different applied systems. We will show that it is perfectly suited for a fast and non-invasive determination of the key rheological properties as given by the frequency dependence of $G'(\omega)$ and $G''(\omega)$.

Experimental set-up

Diffusing Wave Spectroscopy (DWS)

Dynamic light scattering (DLS), or photon correlation spectroscopy (PCS), analyses the fluctuations of the light intensity scattered from a system under study. The light fluctuates due to the local motion of the scatterers. While in conventional light scattering experiments the sample has to be almost transparent (and hence often highly diluted), diffusing wave spectroscopy (DWS) extends “conventional” dynamic light scattering (DLS) to media with strong multiple scattering, treating the transport of light as a diffusion process [12–14]. Analogous to DLS it is possible to express the measured intensity autocorrelation function $g_2(\tau) - 1 = \langle I(t)I(t+\tau) \rangle / \langle I \rangle^2 - 1$ in terms of the mean square displacement of the scattering particle

$$g_2(\tau) - 1 = \left[\int_0^\infty ds P(s) \exp \left(-(s/l^*) k^2 \langle \Delta r^2(\tau) \rangle \right) \right]^2 \quad (1)$$

with $k = 2\pi n/\lambda$ being the wave number of light in a medium with refractive index n . $P(s)$ is the distribution of photon trajectories of length s in the sample and it can be calculated within the diffusion model taking into account the experimental geometry. The transport mean free path l^* characterises the typical step length of the photon random walk, given by the individual particles scattering properties and particle concentration. l^* can be determined independently and enters the analysis as a constant parameter [13]. From Eq. (1) it is possible to numerically calculate the particle mean square displacement $\langle \Delta r^2(\tau) \rangle$ from the measured autocorrelation function $g_2(t)$.

Two-cell technique

To overcome the problem of non-ergodicity in dynamic light scattering [15], arising from the constraint particle motion in a solid like material, we have recently developed a non-invasive efficient new method [6, 7]. We prepare a sandwich consisting of two independent glass cells [thickness $L_2 = L_1 = 1$ mm] where the first cell contains the sample to be investigated, which can be either a stable ergodic or a gelling non-ergodic sample. The second cell, which serves to properly average the signal of the first cell only, contains an ergodic system with very slow internal dynamics and moderate turbidity (Fig. 1). The correlation function $g_2(\tau) - 1$ of the two-cell set-up can be expressed by a product of the correlation functions of the two independent cells

$$g_2(\tau) - 1 = [g_2(\tau, L_1) - 1] \cdot [g_2(\tau, L_2) - 1], \quad (2)$$

which we call the “multiplication rule” [7]. This relation holds if the first layer has a high optical density $L_1/l^* \gg 1$ while the second layer shows only moderate multiple scattering $L_2/l^* \sim 2-3$ [7]. From this it is possible to determine directly the contribution of the first cell $g_2(\tau, L_1) - 1$ by dividing the signal of the two cell sandwich, $g_2(\tau) - 1$, with the separately measured autocorrelation function $g_2(\tau, L_2) - 1$ of the ergodic system in the second cell

$$g_2(\tau, L_1) - 1 = [g_2(\tau) - 1] / [g_2(\tau, L_2) - 1] \quad (3)$$

Multispeckle DWS

Another very useful extension of standard DWS is the use of a CCD camera to follow temporal fluctuations of the scattered light (see Fig. 2). Instead of analysing the fluctuations of intensity at a single spatial position (one speckle spot) we now analyse a large area of the intensity pattern of the scattered light (hence multispeckle) using a

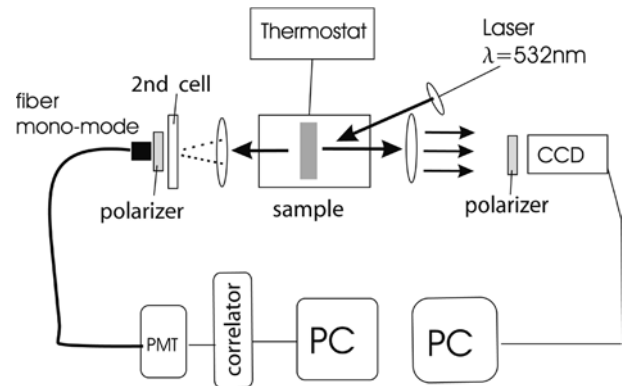


Fig. 1 Schematic plot of the two-cell set-up. The first cell is filled with a liquid or solid-like sample and the second cell is filled with an ergodic system (e.g., polystyrene latex spheres in glycerol)

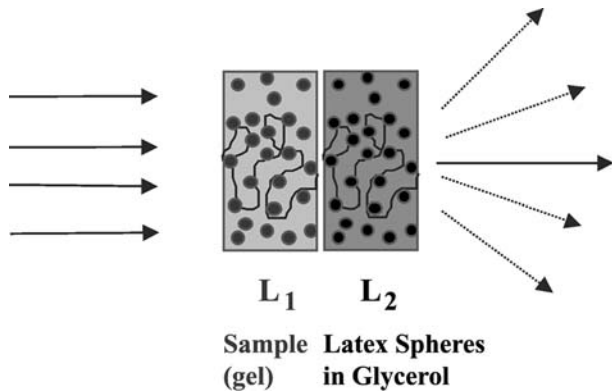


Fig. 2 DWS set-up: an intense laser beam (Verdi from Coherent) is scattered from a turbid sample contained in a temperature controlled water bath. The scattered light is detected in transmission or backscattering with a mono mode fiber or a CCD camera and subsequently analysed digitally (correlator and PC)

CCD camera [4, 11, 17]. The main advantage of this set-up in DWS based microrheology is the significantly improved data acquisition time, since a large number of DWS-scattering experiments is actually performed simultaneously. In standard DWS (or DLS) measurements the data acquisition time has to be several orders of magnitude larger than the typical relaxation time of the correlation function $g_2(\tau)-1$, a restriction that does not apply to multispeckle-DWS. Furthermore, since different configurations of the sample are probed simultaneously the measured correlation function never suffers the problems of non-ergodicity described above.

The main drawback of camera based DWS is the currently still much limited time resolution of CCD cameras. Typically correlation times τ down to approx. 10 ns can be accessed (as compared to 10 ns with a standard photo-multiplier – digital correlator set-up), which is hence not sufficient for most of the fast relaxation processes usually encountered in DWS. However a combination of the novel two-cell technique and multispeckle DWS turns out to be a perfect combination to overcome most of the commonly encountered experimental limitations. Using both techniques enables us to cover a range of 10 ns to at least 10,000 seconds, hence more than twelve orders of magnitude in correlation time [11].

Microrheology

Colloidal gels

Aggregation and gelation in complex fluids has been for a long time a field of intense research where both fundamental as well as applied questions are equally important [5–10, 18, 19]. Applications of gels and sol-gel processing include such different areas as ceramics processing, cosmetics and consumer products, food

technology, to name only a few. Gels are formed by chemical or physical reactions of small sub-units (molecules, polymers or colloids) which can be either reversible or irreversible. The macroscopic features that bring together such different materials are based on the microstructural properties of all gels, which can be described as random networks built up by aggregation of the individual sub-units. Starting from a solution of the sub-units the system is destabilised, which leads to aggregation, cluster formation and gelation. At the gel point a liquid-solid transition is observed which can be characterised by the appearance of a storage modulus in rheological measurements.

We have recently reported the first study of the sol-gel transition in a concentrated colloidal suspensions based on DWS [6]. In our systems a concentrated suspension of monodisperse polystyrene latex spheres is destabilised by increasing the solvent ionic-strength with a catalytic reaction. Thereby the electrostatic repulsion of the double layer is reduced and the particles aggregate due to van-der-Waals attraction. Fig. 3 shows the measured autocorrelation function as

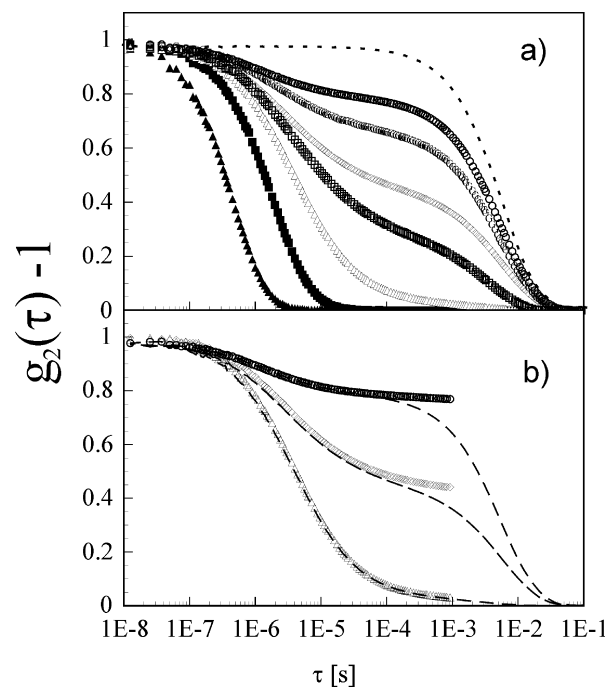


Fig. 3 Sol-gel transition of a concentrated colloidal suspension measured over 10 days with a two-cell set-up (Fig. 2). (a) The destabilised system shows a transition from a liquid state, characterised by an almost exponential decay of the correlation function, to a solid state (*open symbols*) after about 80 min. In the gel-state a continuously increasing plateau builds up in the correlation function, $g_2(\tau)-1$, characteristic for the finite storage modulus of a solid-like system. Dashed line: separately measured autocorrelation function $g_2(\tau, L_2)-1$ of the ergodic system in the second cell. (b) Correlation function of the gel, $g_2(\tau, L_1)-1$, determined from Eq. (3). The dashed lines show uncorrected data, $g_2(\tau)-1$

a function of time ($t=0, 18, 108, 256, 734, 4683, 14,400$ mm). At early stages, clusters form due to particle aggregation and the decay of the correlation function shifts to higher correlation times due to the slower motion of the clusters. Gelation occurs when a single cluster fills the entire sample volume. After the sol-gel transition we observe that the correlation function $g_2(\tau)-1$ does not decay to zero but remains finite (Fig. 3). At the gel time the short time behaviour changes qualitatively from diffusion to a sub-diffusive motion well described by a power law $\langle \Delta r^2(\tau) \rangle \sim \tau^p$ (Fig. 4). We find, within our time resolution, that the exponent for diffusion $p=1$ drops rapidly at the gel point and takes a value of $p \sim 0.7$ for all $t > t_{\text{gel}}$ (see also Fig. 5). Once the gel spans over the whole sample the signal is dominated by a broad distribution of elastic gel modes. In the gel-state the average mean square displacement is well described for all τ by a stretched exponential

$$\langle \Delta r^2(\tau) \rangle = \delta^2 \left[1 - e^{-(\tau/\tau_c)^p} \right], \quad (4)$$

leading to a plateau at long times (with $p \sim 0.7$).

It is also possible to directly link the results from DWS to the macroscopic storage modulus taking advantage of a recent model developed by Krall and Weitz [18]. They found that for the case of fractal (dilute) gels the storage modulus is given by $G' = 6\pi\eta/\tau_c$ [see also Eq. (4)]. Recently we could demonstrate that indeed this macroscopic storage modulus G' deduced from the DWS measurements is in good agreement with classical rheological measurements over a large range of particle concentrations up to 30% volume fraction [8].

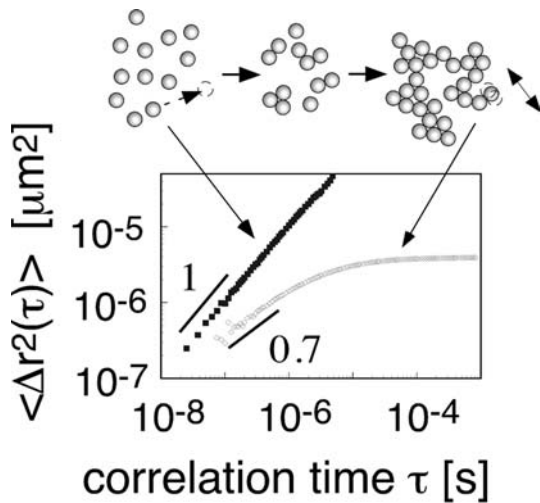


Fig. 4 Particle mean square displacement of a colloidal system from sol to gel determined from Eq. (1)

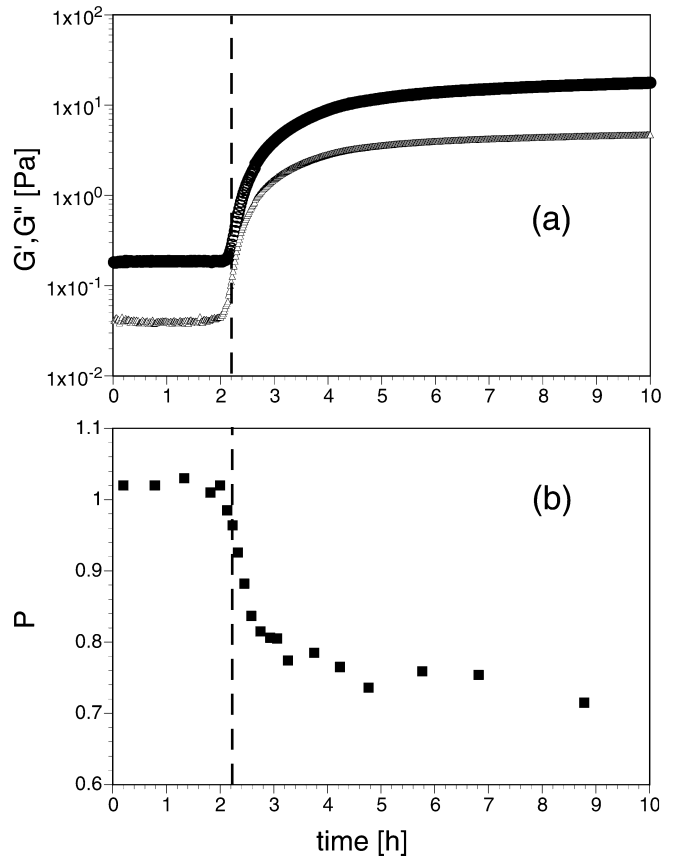


Fig. 5 Comparison of results from classical rheology and DWS during the yogurt making process in fat-free milk. (a) Time evolution of the storage modulus $G'(t)$ (big grey circles) and the loss modulus (small black triangles) obtained from an oscillating rheological measurement (1 Hz, 1% amplitude). (b) Time evolution of the exponent p obtained from DWS

Ceramic slurries and green bodies

Ceramic green bodies can be formed by casting colloidal suspension of high solid loading and then coagulating them in situ with an enzyme catalysed hydrolysis reaction [19]. This forming process is called direct coagulation casting (DCC). The process can be carried out along two different destabilisation routes: a) increasing the ionic strength or b) shifting the pH of the solvent (for details see refs. [5, 6, 19]). Surprisingly it has been found that the mechanical properties of the wet green bodies produced from these two systems appear to be completely different. We have studied the time evolution of the correlation function of destabilised alumina suspension using two-cell DWS. The higher mechanical strength of the ionic strength destabilised system can be clearly identified in the DWS experiments (data not shown). By furthermore analysing the optical density (i.e., $1/l^*$) of the system we could show that the pH destabilised-system is much more homogeneous

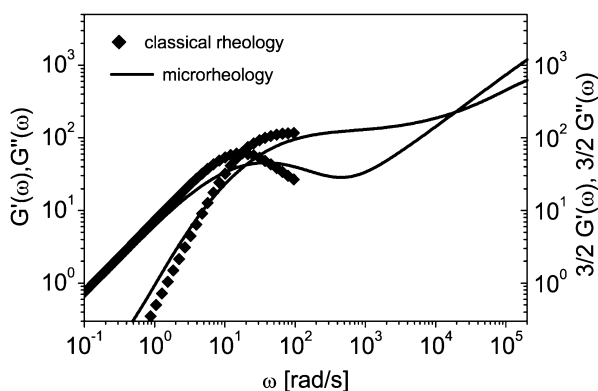


Fig. 6 Frequency dependent elastic moduli obtained from classical rheology (*open symbols*) and DWS based microrheology (*solid line*, right axis). The microrheology results have been multiplied by a factor 3/2 to allow a quantitative comparison of both experiments

which apparently gives rise to the observed different mechanical properties [5].

Biopolymers

Another interesting example is the gelation of casein micellar system in the yoghurt and cheese making process. Fig. 5 shows how DWS can be used to monitor the rheological properties of such a process. We find that the enormous increase in G' and the drop of the exponent coincide (dashed line) demonstrating the link between microscopic particle dynamics and macroscopic sol-gel transition and viscoelastic properties [9, 10].

Concentrated surfactant solutions

The previous examples addressed systems where the scattering particles are part of the system under study.

Now we want to show some very recent measurements where we have introduced tracer particles (polystyrene spheres, diameter 720 nm) in an otherwise transparent matrix consisting of a concentrated surfactant solution. Under the chosen conditions these surfactants form giant, polymer like, micelles, which results in a surprisingly strong viscoelastic liquid [20]. In this case we can take advantage of the formalisms derived for tracer-microrheology which allows to link directly the particle mean square displacement, as obtained from DWS, to the macroscopic viscoelastic moduli $G'(\omega)$, $G''(\omega)$ [1–3]. Fig. 6 shows the excellent agreement between classical rheology and DWS based microrheology, with a dramatically increased frequency range for the latter technique [11]. For a quantitative comparison a scaling factor of 3/2 has been introduced. The origin of this factor is not well understood yet but, as we think, it likely reflects the coupling of the tracer sphere to the medium not well described by current theoretical approaches (see also [3, 11]).

Conclusions

In conclusion, we have shown that DWS based microrheology is a versatile tool to study and characterise the rheological properties of complex fluids and gels. With the advent of new techniques such as the two-cell method and the use of CCD cameras for slow relaxation processes it is now possible to study an increasingly large number of liquid and solid-like complex media. This is expected to have an equally strong impact on both applied and fundamental research. In particular the fast and non-invasive way the information can be obtained from laser light scattering should make these optical techniques an ideal method for industrial applications, e.g., for system characterisation and process monitoring.

References

- Mason TG, Weitz DA (1995) Phys Rev Lett 74:1250; Mason TG, Gang HU, Weitz DA (1997) Opt Soc Am A 14(1):139
- Gittes F, Schnurr B, Olmsted PD, MacKintosh FC, Schmidt CF (1997) Phys Rev Lett 79:3286
- Levine AJ, Lubensky TC (2000) Phys Rev Lett 85:1774
- Knaebel A, Bellour M, Munch J-P, Viasnoff V, Lequeux F, Harden JL (2000) Europhys Lett 52:73–79
- Wyss H, Romer S, Scheffold F, Schurtenberger P, Gauckler LJ (2001) J Coll Interface Sci 241:89–97
- Romer S, Scheffold F, Schurtenberger P (2000) Phys Rev Lett 85:4980
- Scheffold F, Skipetrov SE, Romer S, Schurtenberger P (2001) Phys Rev E 63:61404
- Romer S, Bissig H, Trappe V, Scheffold F, Schurtenberger P (in preparation)
- Schurtenberger P, Stradner A, Romer S, Urban C, Scheffold F (2001) CHIMIA 55:155–159
- Romer S, Urban C, Stradner A, Kruijff CG de, Schurtenberger P (2003) Food Hydrocoll (submitted)
- Cardinaux F, Cipelletti L, Scheffold F, Schurtenberger P (2003) (submitted)
- Maret G, Wolf PE (1987) Z Phys B 65:409
- Pine DJ, Weitz DA, Chaikin PM, Herbolzheimer E (1988) Phys Rev Lett 60:1134
- Weitz DA, Pine DJ (1993) In: Brown W (ed.) Dynamic light scattering. Oxford University Press, New York

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15. Xue JZ, Pine DJ, Milner ST, Wu XL, Chaikin PM (1992) *Phys Rev A* 46:6550; Pusey PN, Megen W van (1989) *Physica A* 157:705
 16. Romer S, Scheffold F, Schurtenberger P (2000) Suisse Institute of Intellectual Property, patent application filed 27th February 2000 under number 200 0335/00
 17. Cipelletti L, Weitz DA (1999) *Rev Sci Instrum* 70:3214
 18. Krall AH, Weitz DA (1998) *Phys Rev Lett* 80:778
 19. Graule TJ, Baader FH, Gauckler LJ (1994) *J Mater Educ* 16:243
 20. Cannavacciuolo L, Sommer C, Pedersen JS, Schurtenberger P (2000) *Phys Rev E* 62:5409–5419; Sommer C (2001) PhD thesis, ETH Zürich