Strain hardening of fractal colloidal gels

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Abstract

We report on experiments on the rheology of gels formed by diffusion-limited aggregation of neutrally buoyant colloidal particles. These gels form very weak solids, with the elastic modulus, $G'(\omega)$, larger than the loss modulus, $G''(\omega)$, and with both $G'(\omega)$ and $G''(\omega)$ exhibiting only a very weak frequency dependence. Upon small but finite strains $\gamma < 0.45$ the elastic modulus increases roughly exponentially with the square of the strain; we quantitatively account for the observed strain hardening with a model for the highly non-linear elastic response of a single backbone segment to elongational deformation resulting from the unravelling of backbone contortions.

81.40.Jj, 82.70.Dd, 82.70.Gg, 83.50.Gd

Colloidal particles aggregating by attractive interactions form disordered, highly ramified clusters; however, despite their apparent complexity, these structures are on average self-similar and the mass of a cluster, M, is related to its radius R by $M(R) \sim M_0(R/a)^{d_f}$, where M_0 is the mass of the colloidal monomer whose size is a [1]. The fractal mass exponent d_f characterizes the ramification of the cluster and varies between $d_f = 2.1$ for reaction-limited cluster aggregation and $d_f = 1.8$ for diffusion-limited cluster aggregation (DLCA) [2]. In the latter case the distribution of cluster sizes is fairly narrow and the characteristic cluster size grows linearly with time. Aggregation of clusters eventually leads to a space-filling structure which is no longer fractal on all length scales but which can instead show long-range correlations as revealed by a scattering peak corresponding to a characteristic cluster size $R_c = a\varphi^{1/(d_f-3)}$, where φ is the initial volume fraction of monomer particles [3,4]. The clusters themselves are close packed, forming a ramified, tenuous gel structure. This structure should be an elastic material with unique properties, which are determined not only by d_f, but also by the connectivity or chemical dimension, d_b, which characterizes the scaling of the contour length within the cluster. Since the clusters making up the gel are fractal, and hence very tenuous, the elasticity can be expected to be extremely weak, but should increase dramatically with increasing φ. Since the backbone is contorted, a shear strain will be accommodated by a straightening of the backbone, stretching out the inherent bends. This should lead to highly unusual elastic properties; the stretching of the backbone will increase its rigidity and thus the gel can be expected to exhibit pronounced strain hardening, becoming stiffer as it is stretched, until it catastrophically breaks. However, because of the very weak elasticity, and the difficulty of working with completely unsheared, virgin gels, this interesting behavior has never been observed.

By contrast, strain hardening has been observed in a completely different class of material, semiflexible biopolymers such as cellulose [5,6], F-actin [7] and vimentin [8]. Such polymers are responsible for the mechanical stability of biological tissues. However, the origin of the strain hardening in these systems remains obscure, in part due to a lack of knowledge about the detailed network structure, and the role of chemical crosslinks. Although they

differ in the details of their structure, these polymer networks share an essential feature with colloidal aggregate gels: locally they each consist of segments with significant bending rigidity, which dominates their elastic properties. Thus, an understanding of the elasticity and strain hardening of colloidal gels may also provide important insight into the properties of these biopolymer networks.

In this paper, we present measurements of the elastic properties of virgin colloidal aggregate gels. We show that their very weak elasticity increases as $\varphi^{3.2}$, in agreement with theoretical expectations for a fractal network. In addition, we also show that the gels do indeed exhibit a pronounced strain hardening before they catastrophically break. Surprisingly, the data can all be scaled onto a single master curve, independent of φ. We quantitatively account for this strain hardening and the observed scaling using a model that predicts the non-linear stress response of a network of randomly oriented backbones of connected clusters.

We use polystyrene latex particles with diameter $2a = 19\,\mathrm{nm}$ in a neutrally buoyant mixture of H_2O and D_2O [3,9] at 25°C; adjusting the density of the solvent to the particle density is necessary to suppress sedimentation which leads to either compactification of clusters and more rigid structures (work hardening), or, at larger stresses, breakage of bonds before clusters touch each other (brittle regime) [10]. We initiate aggregation by addition of $MgCl_2$ to a concentration of 6 mM; with initial volume fractions $4.6\cdot10^{-3} \leq \varphi \leq 1.58\cdot10^{-2}$, gels form within several hours, leading to macroscopically homogeneous structures. Static light scattering [4,9,11] from these gels at lower φ confirms $d_\mathrm{f} \sim 1.9$, slightly above the value expected for DLCA, and consistent with the initial aggregation being in the intermediate regime between diffusion- and reaction-limited cluster aggregation; we note, however, that diffusion still dominates at longer times, leading to a well defined average cluster size.

We measure the linear storage and loss moduli G' and G'' with a controlled-strain rheometer in an oscillatory shear experiment using a double-wall-Couette geometry. The gels are allowed to fully form in the rheometer cell, ensuring that we measure the properties of the undisturbed gel. Typical examples of the frequency-dependent G' and G'' are shown in Fig. 1, for a gel with $\varphi = 8.9\cdot10^{-3}$, and using a strain amplitude $\gamma = 8\cdot10^{-3}$; reducing γ yielded

the same values of $G'(\omega)$ and $G''(\omega)$, confirming linearity. The storage modulus is about an order of magnitude larger than the loss modulus, and is only very weakly dependent on frequency; this is consistent with the formation of a solid gel structure. The loss modulus is also nearly independent of frequency, except at the very lowest frequencies probed, where a small increase indicates persistent loss mechanisms presumably indicative of very slow rearrangements within the gel; we emphasize however, that these rearrangements occur on a time scale that is many orders of magnitude slower than the measurement time.

The dependence of G' on φ is shown in Fig. 2. We find a power-law scaling $G'(\varphi) \sim \varphi^{\nu}$, comparable with indirect measurements using compactive strength [12]. The strong φ-dependence of G' provides considerable insight into the nature of the elasticity of these gel networks. To account for this behavior, we assume that the modulus is determined by the spring constant of the backbone of the average cluster. The spring constant of a loopless fractal is size dependent, and is given by $k(R) = k_0\,(R/a)^{-(2+d_{\rm b})}$ [13], where k_0 is the bending spring constant associated with an elementary bond. This expression reflects the fact that the extension of a fractal cluster occurs through the unbending of the contorted path of the chain; thus the spring constant decreases as the cluster size increases and contortions become easier to unbend. The spring constant depends inversely on the cross-sectional area of the chains, assumed to be R^2, and inversely on the longitudinal chemical length, $R^{d_{\rm b}}$. The elastic modulus of the gel is then $G' = k(R_{\rm c})/R_{\rm c}$, yielding an exponent of $\nu = (3+d_{\rm b})/(3-d_{\rm f})$ [14]. Experimentally, we find $\nu = 3.2 \pm 0.3$; given the sensitivity of ν to $d_{\rm f}$, this is in excellent agreement with the predicted value, which is between 3.2 and 3.7 for $d_{\rm f}$ between 1.9 and 2, and using $d_{\rm b} = 1.1$, obtained from computer simulations [15]. In addition, at the lowest volume fractions, the magnitude of G' agrees very well with the value determined from dynamic light scattering [9].

The fractal structure and connectivity suggests another important consequence for the elastic properties of the gel; as the network is strained, and the inherent bends are removed, we expect a rapid *increase* in the elastic modulus with increasing strain. We test for this using a series of gels of different φ by measuring the dependence of G' and G'' on the

maximum strain γ of an oscillatory measurement at a fixed frequency of 10 rad/s. As shown in Fig. 3, we observe a linear response for $\gamma < 0.1$, where both G' and G'' are independent of γ. Further increase in strain amplitude results in a very rapid increase in G' and G'', up to $\gamma \approx 0.45$ above which both moduli drop precipitously; larger strains are no longer recoverable, indicating irreversible breakage of bonds between clusters. The behavior of these gels is in strong contrast to the marked shear thinning observed in weakly flocculated suspensions where both G' and G'' decrease above a yield strain which is strongly dependent on volume fraction [16].

To account for the strain hardening, we consider the effects of a large strain on a single, stress-bearing segment of the network, and average the contributions from randomly oriented segments. In a randomly connected network, shear stress is accommodated by a longitudinal stretching of the strands that form the backbone. A large longitudinal strain, λ, stretches an individual strand, pulling out the bends that govern its elasticity, and making it anisotropic in shape by increasing its length while decreasing its width. This drastically modifies its elastic constant, which is now characterized in terms of the new width, ξ. Expressing the strain as $\lambda = g\xi/R_c$, where $g = (R_c/\xi)^{d_b}$ is the number of blobs of size ξ, the new width is $\xi = R_c\lambda^{1/(1-d_b)}$. Then, the spring constant of the extended strand is given by that of g springs in series, yielding $k(\lambda R_c) = k_0\,(R_c/a)^{-(2+d_b)}\lambda^{2/(d_b-1)}$. This spring constant is very sensitive to the strain, λ, for typical values of d_b, which are close to unity for these fractal aggregates [15]. The force required to stretch a backbone segment by a factor λ is

$$f(\lambda) = k_0 a\,(R_c/a)^{-1-d_b}\left[\lambda^A - 1\right] \tag{1}$$

where $A = (1+d_b)/(d_b-1)$.

The strain dependence of this force leads to the strain hardening of the modulus. To calculate this, we assume that the deformation is affine, characterized by the deformation tensor Λ. Backbone strands are then both stretched and rotated by Λ, and the magnitude of λ for any chain depends on its orientation $\mathbf{n}$ with respect to the principal axes of the deformation tensor, $\lambda = |\Lambda\mathbf{n}|$. The force along a strand is $\Lambda\mathbf{n}/|\Lambda\mathbf{n}|\,f(|\Lambda\mathbf{n}|)$, from which the

total stress is calculated as

$$\sigma = \frac{1}{R_c^2} \int \mathrm{d}^2\mathbf{n}\, \Lambda\mathbf{n}\, \frac{\Lambda\mathbf{n}}{|\Lambda\mathbf{n}|}\, f(|\Lambda\mathbf{n}|) \tag{2}$$

where we have assumed a uniform distribution of strand orientations. When $d_b \approx 1$, extensional stresses dominate over contributions from compression and rotation; the force along a direction $\Lambda\mathbf{n}$ may then be approximated as $\mathbf{n} f(|\Lambda\mathbf{n}|)$, resulting in

$$\sigma_{xy} = \frac{1}{R_c^2} \int\int \sin\theta\, \mathrm{d}\theta\, \mathrm{d}\phi\, \sin^2\theta\, \sin 2\phi\, f(\lambda(\theta,\phi)) \tag{3}$$

In the case of a simple shear along the x-axis with a strain γ the extension ratio is $\lambda(\theta,\phi) = \left(1 + \gamma \sin^2\theta\, \sin 2\phi + \gamma^2 \sin^2\theta \cos^2\phi\right)^{1/2}$ and the force becomes

$$f(\lambda) = L\, \left[1 + \gamma \sin^2\theta \sin 2\phi + \gamma^2 \sin^2\theta \cos^2\phi\right]^{A/2} - L \tag{4}$$

$$\sim L\, \exp\left[\frac{A\gamma}{2} \sin^2\theta \sin 2\phi + \frac{A\gamma^2}{2} \sin^2\theta \cos^2\phi\right] - L \tag{5}$$

where $L = k_0\, a\, (R_c/a)^{-1-d_b}$. For large values of A ($d_b \approx 1$), there is a regime where terms quadratic in γ^2 are small. We neglect the quadratic term, integrate over all orientations with Eq. 3, and expand the exponential terms; then using $G' = \sigma_{xy}/\gamma$ we obtain

$$G'(\gamma) = \frac{LA}{R_c^2} \sum_{n=0}^{\infty} \frac{1}{(2n+1)!} I_{4n+5} I_{2n+2} \left(\frac{A\gamma}{2}\right)^{2n} \tag{6}$$

where $I_l = \int_0^{2\pi} \mathrm{d}\theta\, \sin^l\theta$.

This result has an important consequence; Eq. 6 suggests that scaling individual $G'(\gamma)$ curves at different volume fractions with their value at zero strain should yield a master curve for the excess elastic modulus that is independent of φ. We test this prediction in Fig. 4, where we plot all our data, rescaled by the modulus at small strain amplitudes, as a function of γ; the data do indeed follow the predicted scaling. Moreover, as shown by the solid curve, we obtain excellent agreement with the prediction Eq. 6 for $G'(\gamma)$ for all φ if we adjust the backbone dimension d_b to 1.07, a value which is consistent with the scaling of the zero-strain elastic modulus with volume fraction. This value is also in remarkably good agreement with the results of computer simulations [15].

Surprisingly, the stress response in the oscillatory shear experiments is remarkably linear, as measured by small third-harmonic stress components; on the other hand, we observe that the strains are not recoverable. This suggests that small but finite deformations lead to formation of contacts between side-chains which now become part of the stress-conducting network; as the strain is released, these newly formed backbone segments either buckle or deform; deformation, however, counteracts the complete recoil of stretched segments belonging to the original network, leading to an enhanced modulus at zero extension. Upon further extension, the stress response is now mainly due to the first-generation backbone segments since their extension is large. This is consistent with the observation that the observed scaling of $G'(\gamma)$ with γ is somewhat steeper than we would expect using the predicted expansion coefficients.

The importance of buckling events is also revealed by the loss modulus: at fixed strain amplitude, $G''(\omega)$ is almost independent of frequency, suggesting that energy dissipation arises from displacements rather than from coupling to velocities that would depend on strain rates (i. e. $\gamma\omega$ in an oscillatory experiment.) Then during each oscillation cycle, a constant fraction of the work stored in the deformed network is lost in conformational changes occurring locally on the length scale of a network segment, leading to a constant loss tangent G''/G'; indeed, we also find that the loss tangent is practically independent of the strain amplitude.

Unlike the nonlinear elasticity of rubbers which is governed by entropic restoring forces [17], elasticity and strain hardening in fractal colloidal gels have their origin in the intrinsic stiffness of contorted backbone segments, even in the absence of thermal fluctuations; increasing strain straightens the contorted path, resulting in an increase in the elastic modulus. Fractal colloidal gels might thus be useful model systems for the study of strain hardening in other random networks that are governed by bending stiffness, such as F-actin whose segment dynamics show remarkable similarities to colloidal gels [18]. Elasticity and strain hardening in fractal colloidal gels relies critically on the existence of a continuous network of permanent bonds; the origin of elasticity in networks of semiflexible polymers, on the other

hand, remains highly controversial, in part due to the poorly elucidated role of permanent chemical crosslinks which are presumably important for linear viscoelasticity as well as for the response to large strains. The detailed description of strain hardening presented here may provide a possible starting point for any model of semiflexible polymers; it certainly provides an excellent account of the behavior of colloidal aggregate gels.

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FIGURES

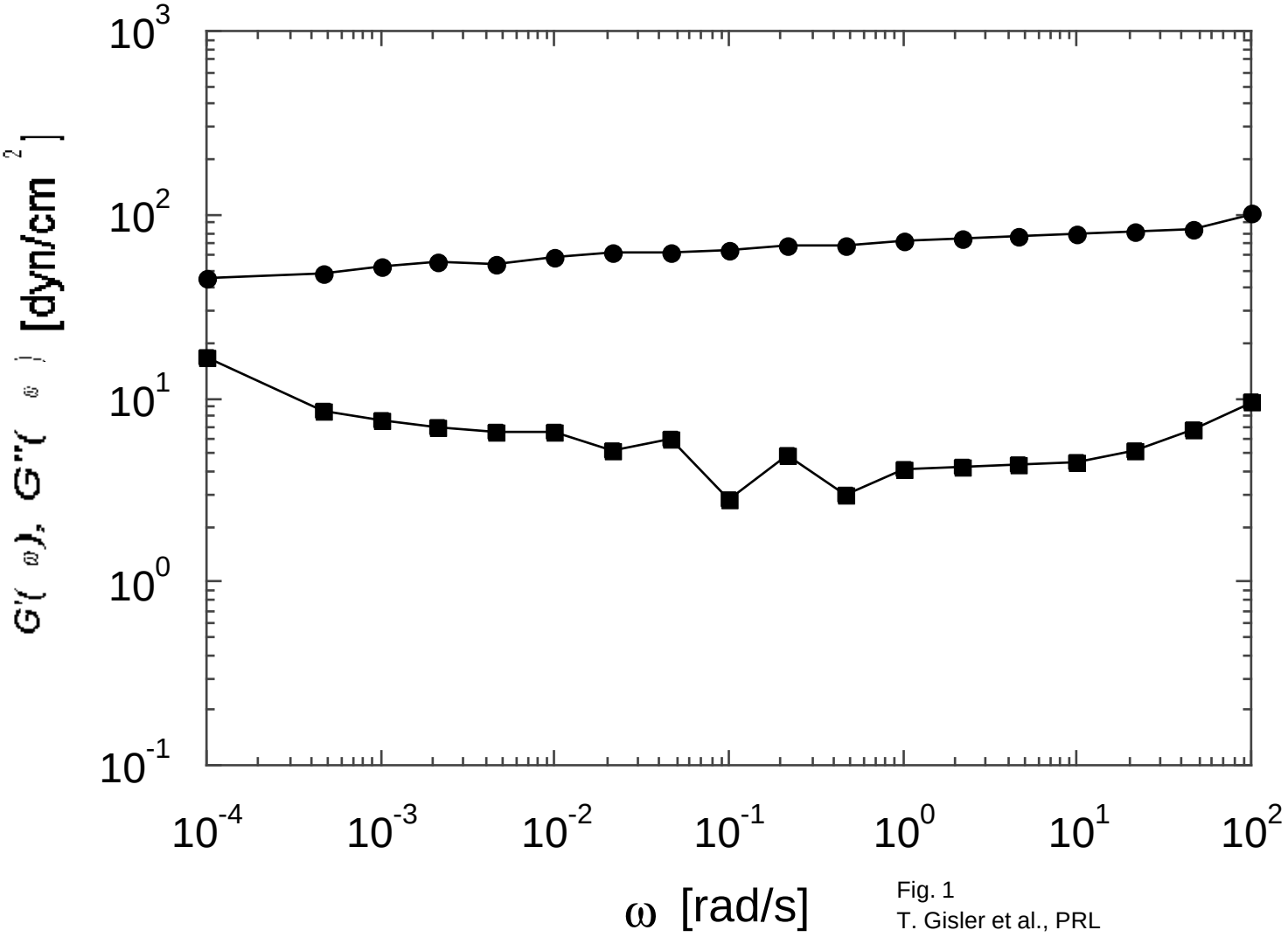

FIG. 1. Linear storage modulus $G'(\omega)$ (circles) and loss modulus $G''(\omega)$ (squares) as a function of angular frequency ω at volume fraction $\varphi = 8.9 \cdot 10^{-3}$ after full gelation of clusters. The strain amplitude of the oscillatory shear was $\gamma = 8 \cdot 10^{-3}$.

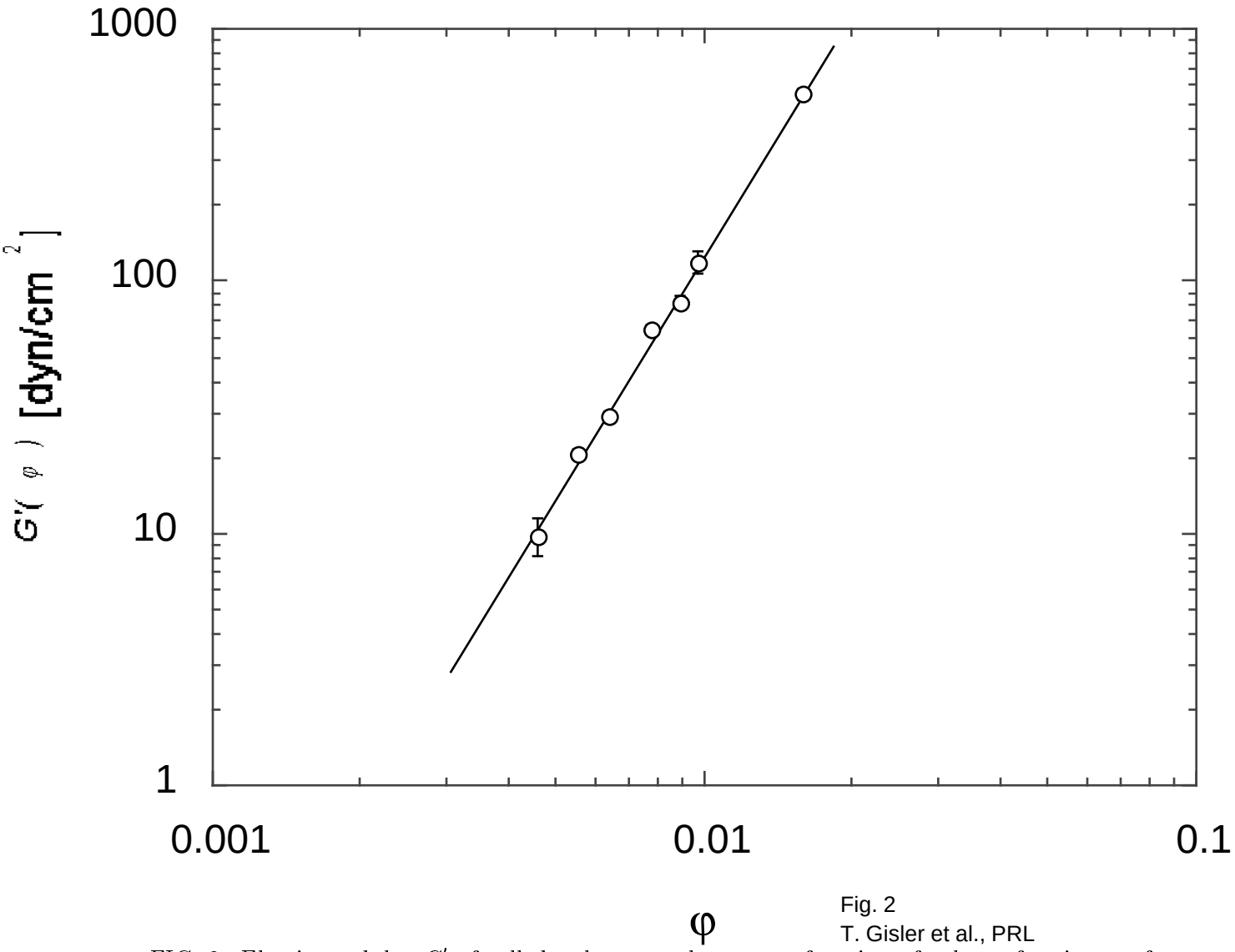

Fig. 2
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FIG. 2. Elastic modulus G' of gelled polystyrene latex as a function of volume fraction φ of primary particles, measured at small strain amplitudes $8 \cdot 10^{-4} \leq \gamma \leq 8 \cdot 10^{-3}$. The modulus scales as a power law $G' \sim \varphi^{\nu}$, with an exponent $\nu \approx 3.2$ (full line); this value is consistent with the prediction $\nu = (3 + d_{\mathrm{b}})/(3 - d_{\mathrm{f}}) = 3.73$ using $d_{\mathrm{f}} = 1.9$ determined by static light scattering and a value for the backbone dimension $d_{\mathrm{b}} = 1.1$ for diffusion-limited aggregation.

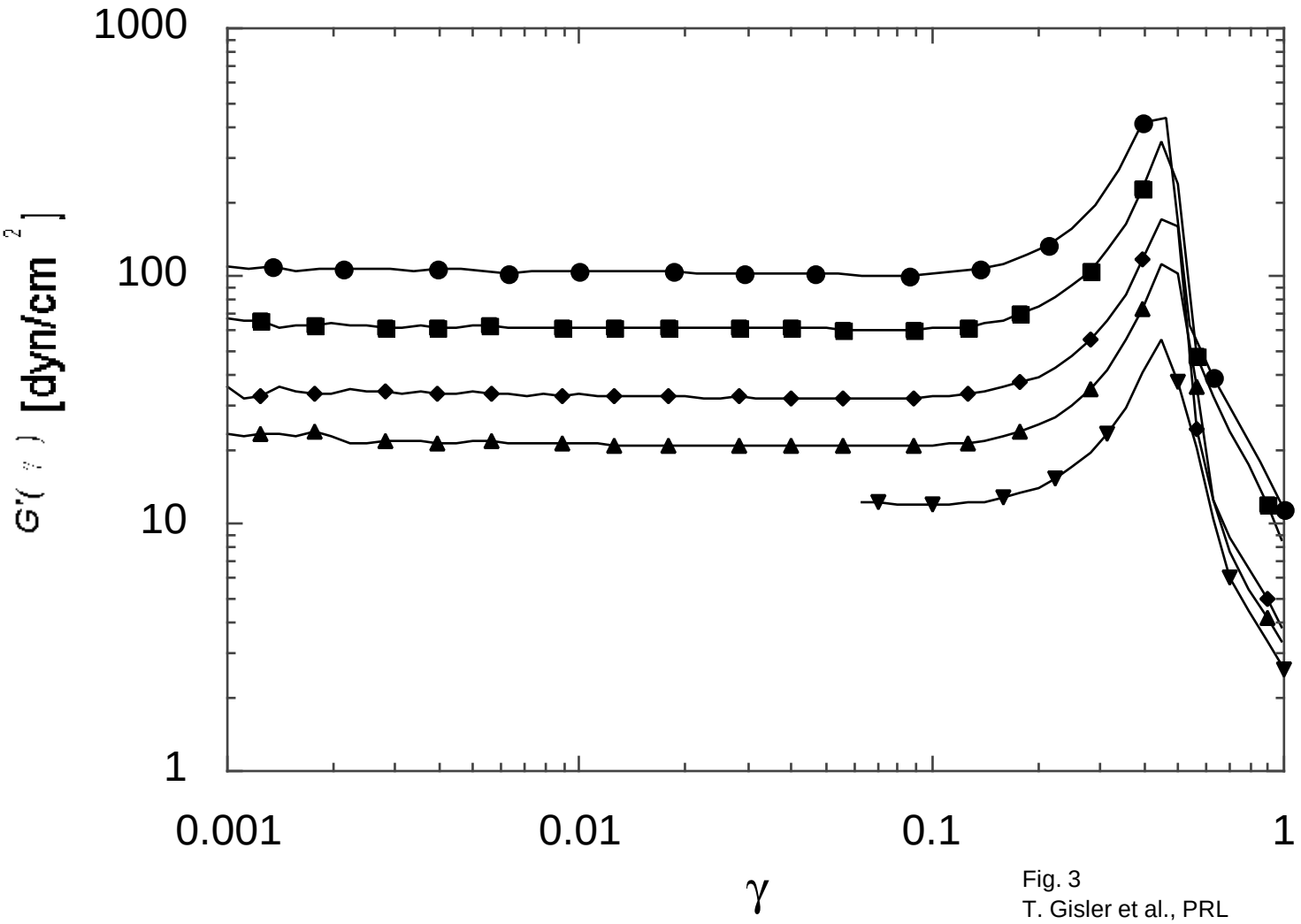

Fig. 3
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FIG. 3. Elastic modulus G' as a function of the strain amplitude γ in an oscillatory shear experiment. Volume fractions are $\varphi = 9.7{\cdot}10^{-3}$(•), $\varphi = 7.8{\cdot}10^{-3}$(■), $\varphi = 6.4{\cdot}10^{-3}$(⧫), $\varphi = 5.5{\cdot}10^{-3}$(▲) and $\varphi = 4.6 \cdot 10^{-3}$(▼). The excitation frequency is 10 rad/s. Strains beyond $\gamma \approx 0.45$ result in (irreversible) breakage of the backbone.

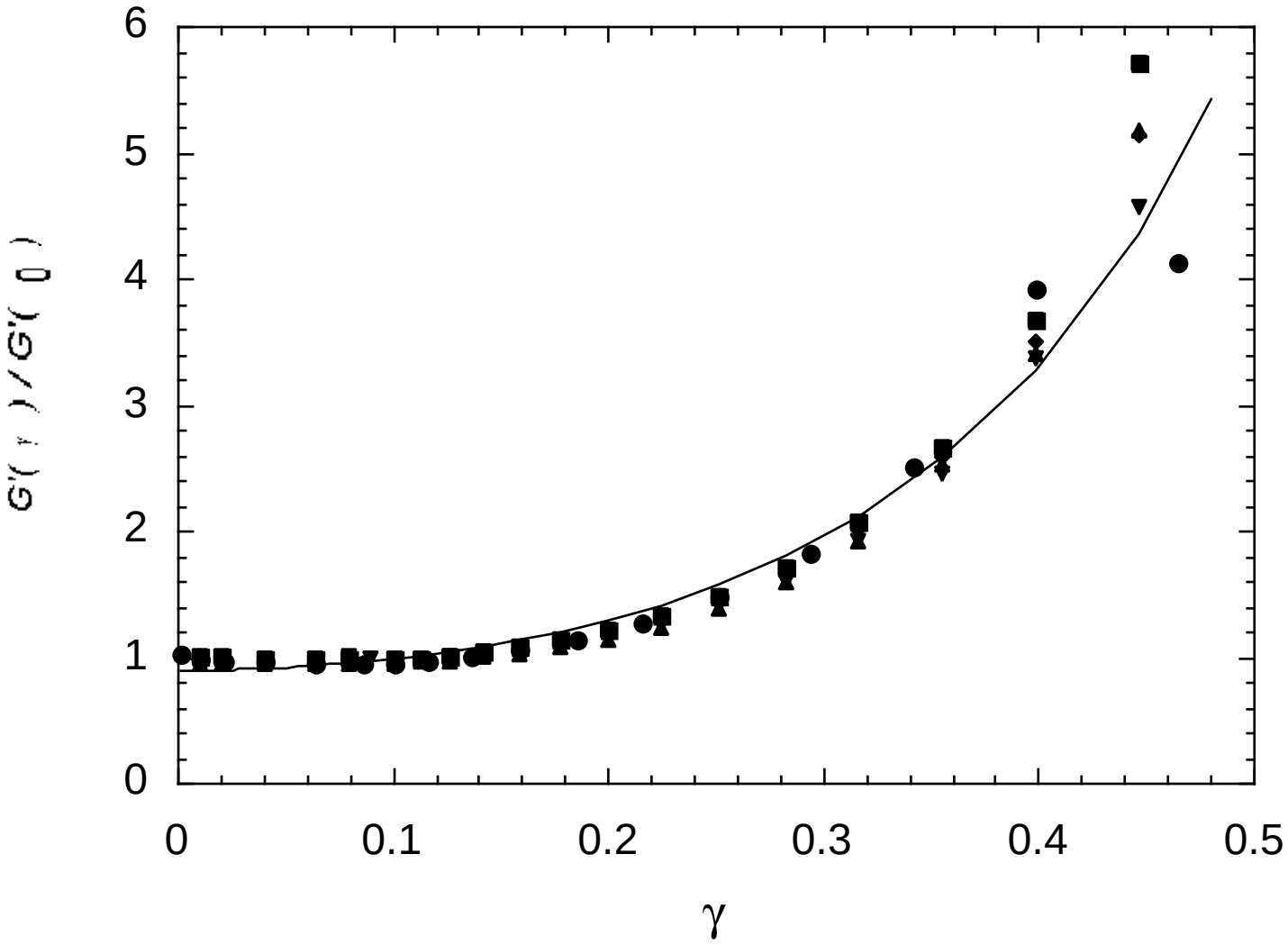

Fig. 4
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FIG. 4. Elastic modulus $G'(\gamma)$ scaled with the zero-strain modulus $G'(0)$ as a function of γ in an oscillatory shear experiment. Symbols denote different volume fractions of monomers (see Fig. 3). The full line shows a fit of a fourth-order power series in γ^2, using the theoretical expansion factors (see Eq. 6); the value of the backbone dimension was adjusted to $d_{\rm b} = 1.07$, consistent with the dependence of the zero-strain elastic modulus on volume fraction.