

## Bulk and shear moduli of compressed microgel suspensions

Juan José Liétor-Santos, Benjamín Sierra-Martín,<sup>\*</sup> and Alberto Fernández-Nieves  
*School of Physics, Georgia Institute of Technology, Atlanta, Georgia 30332-0430, USA*

(Received 29 April 2011; published 8 December 2011)

We independently determine the bulk and shear moduli of compressed microgel suspensions and the bulk modulus of individual microgel particles and find that the elastic behavior of the suspension reflects the degree of compression of the particles. This feature, which is distinct from other soft materials such as emulsions or foams, can give rise to an unusually large difference between the bulk and shear moduli of the suspension. Our results extend our understanding of soft materials to systems based on compressible objects, opening up possibilities for engineering materials with drastically different responses to shear and compression.

DOI: [10.1103/PhysRevE.84.060402](https://doi.org/10.1103/PhysRevE.84.060402)

PACS number(s): 83.80.Hj, 47.57.Qk, 83.80.Kn

Shearing is typically easier to achieve than compression. For example, the speed of sound in solids is larger for longitudinal waves than it is for transverse waves, reflecting the larger bulk modulus of a solid material compared to its shear modulus. The ratio between these speeds, however, is generally small,  $\sim 2$  [1]. Alternatively, consider solid-solid friction. From experience, we know that the friction force  $f$  is proportional to the normal force  $N$  via the so-called friction coefficient  $\mu$ , which is typically within the range  $0.1 < \mu < 1$  [2]. As a result,  $f$  is at most approximately an order of magnitude smaller than  $N$ , reflecting in large measure the difference between shearing or compressing the *springs* mediating the interaction between the atoms in the two solids in contact.

Disordered soft materials, such as emulsions and foams, also reflect this difference. These systems comprise drops or bubbles, which, above random close packing, are no longer spherical but rather have flat areas in the contact region between neighbors; this flattening increases with volume fraction  $\phi$ , leading to an increased surface area and thus to an increased interfacial energy, which in turn leads to elastic behavior [3,4]. As for most other elastic solids, compressed emulsions and foams are easier to shear than to compress. For emulsions, the bulk modulus  $K$  and the shear modulus  $G'$  have similar  $\phi$ -dependencies, with  $G'/K \approx 0.1$  for  $0.62 \lesssim \phi \lesssim 0.85$  [3]. For dry and wet foams, recent experimental and modeling results show that  $G'/K \approx 0.7$  [5,6]. Interestingly, the drops and bubbles in these disordered solids do not change volume as  $\phi$  increases. The elasticity then results from how the shapes of the drops and bubbles changes with  $\phi$ . This is recasted by modeling the contact region between neighbors with springs [7]. Depending on the degree of packing, these hypothetical springs are more or less compressed, resulting in comparable shear and bulk moduli. In the case of emulsions, there is a threshold  $\phi$  value for this. When  $\phi \gtrsim 0.85$ , the osmotic pressure, and consequently  $K$ , increases faster than  $G'$  to eventually diverge at  $\phi \rightarrow 1$ ; this simply results from the incompressibility of liquids [8,9]. Remarkably, when the constituent elements making the system are compressible, the relevant microscopic measure determining the macroscopic mechanical behavior is not so well understood [10]. This is the

case for suspensions based on microgel particles, which are cross-linked polymer networks in the colloidal-size domain. Within a narrow  $\phi$  range, the elasticity of these suspensions is reminiscent of the elasticity of emulsions, provided the Laplace pressure in the latter is replaced by a contact modulus related to the Young's modulus of the particle [11]. This analogy, however, breaks down as soon as the particle number density forces the shrinkage of the microgel particles. In this regime, it has been proposed that the elasticity of the suspension is controlled by some local elasticity obtained by measuring the mean-square displacement of colloids embedded in the microgel suspension [12], by the individual particle bulk [13] or shear [14] modulus, or by the cross-link density [15]; this indicates that the relevant elastic scale of these systems remains unknown.

In this Rapid Communication, we show that the microgel bulk modulus determines the  $\phi$  dependence of the bulk and shear modulus of the suspension. Interestingly, we find that  $K$  is three orders of magnitude larger than  $G'$ , in contrast to what is generally observed for most materials. Our results elucidate the role of single-particle compressibility. This will enable a more complete picture of how soft materials respond to external stresses, ultimately enabling the use of this parameter to design materials that can exhibit different responses to shear and compression.

We use microgel particles comprising vinylpyridine (VP), a weak base that ionizes at  $pH$  below  $\sim 4$ , and divinylbenzene (DVB), a cross-linker [16]. We make two set of particles with different DVB concentrations, 0.5 and 1.3 wt %, to explore the influence of particle stiffness. Suspensions are kept at  $pH = 3$  through addition of HCl. At this  $pH$ , the particles are fully swollen; their radii are  $a = 510$  nm for 0.5 wt % DVB and  $a = 350$  nm for 1.3 wt % DVB. Noteworthy, since these particles can change volume for sufficiently high particle concentrations, we use a generalized volume fraction  $\zeta$  to characterize the state of the system [17]:  $\zeta = nV_o$ , with  $n$  the particle number density and  $V_o$  the volume of a particle measured at low concentration. We note that random organizations of microgels can have  $\zeta$  values much larger than 0.64. In this concentration region, the value of  $\zeta$  reflects the degree of deformation of the particles with respect to the preferred low-concentration, swollen state.

We measure the osmotic pressure  $\Pi$  of both microgel suspensions as a function of  $\zeta$  using a membrane osmometer and find that  $\Pi$  increases with  $\zeta$ . In addition,  $\Pi$  is larger

<sup>\*</sup>Present address: Department of Applied Physics, University of Almería, Spain, 04120.

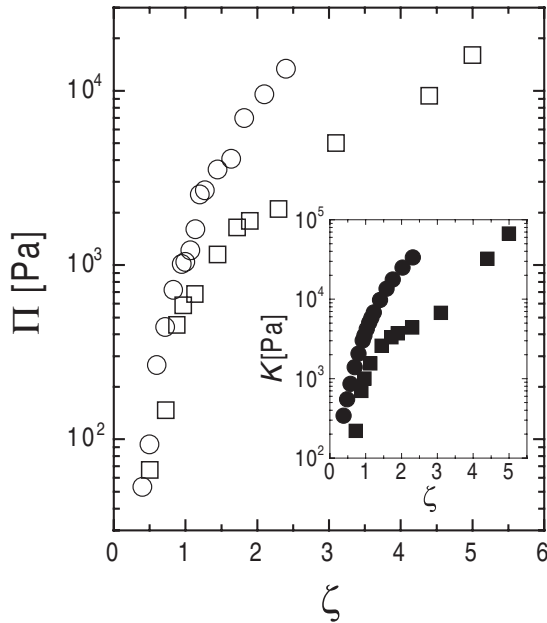


FIG. 1. Osmotic pressure vs  $\zeta$  for microgel suspensions comprising particles with ( $\square$ ) 0.5 wt % DVB and ( $\circ$ ) 1.3 wt % DVB. The inset shows the corresponding bulk modulus of the suspension calculated using  $K = \zeta \frac{d\Pi}{d\zeta}$ .

for the suspension made of the more cross-linked microgels, as shown in Fig. 1; since the particle size decreases with cross-link amount, a larger number of particles is required to attain a certain value of  $\zeta$ . From these measurements, we obtain the suspension bulk modulus or inverse compressibility:  $K = \zeta \frac{d\Pi}{d\zeta}$ . Reminiscent of the osmotic pressure behavior, we find that  $K$  increases with  $\zeta$  and that  $K$  is larger for the suspension comprising the more cross-linked microgels, as shown in the inset of Fig. 1. This suggests that, at least for  $\zeta \gtrsim 1$ , where the particles must be compressed by their neighbors, the bulk modulus of the suspension is determined by the bulk modulus of the individual microgels, consistent with previous suggestions [13].

To test this hypothesis, we mix a dilute suspension of microgel particles with a dextran solution of known osmotic pressure  $\Pi_d$  and quantify how the microgels deswell with increasing osmotic pressure using dynamic light scattering [18]. This allows the determination of the bulk modulus of individual microgels  $K_p$ . For low dextran osmotic pressure, the microgel volume  $V$  remains essentially constant, indicating that the imposed osmotic pressure is smaller than the particle bulk modulus. Deswelling begins when  $\Pi_d \approx K_p$  [19]. In this region,  $V$  decreases with increasing  $\Pi_d$ , as shown in Fig. 2(a). We obtain  $K_p$  from the slopes of the  $\Pi_d$ - $V$  curves by using  $K_p = -V \left( \frac{d\Pi_d}{dV} \right)$ . We find  $K_p = (1.6 \pm 0.1)$  kPa for the stiffer microgels and  $K_p = (0.40 \pm 0.02)$  kPa for the softer microgels, in their respective swollen states. As the particles shrink,  $K_p$  concomitantly increases, as shown in Fig. 2(b).

We then normalize both the suspension osmotic pressure and bulk modulus with  $K_p$ . For  $\zeta \leq 1$ , we use the bulk modulus of swollen microgels. For  $\zeta > 1$ , however, we model the required microgel shrinkage by assuming that  $V \sim 1/\zeta$ , and

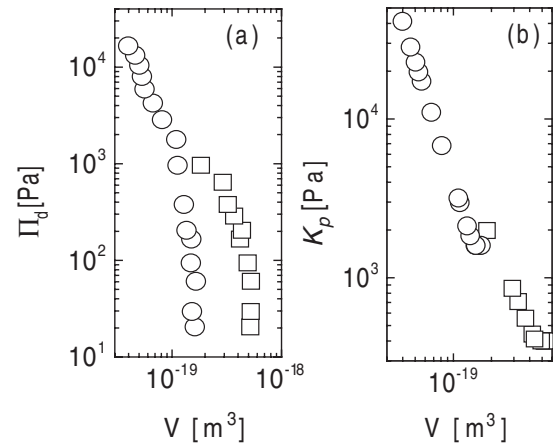


FIG. 2. (a) Dextran osmotic pressure and (b) bulk modulus of individual microgels vs the volume of the particles. ( $\square$ ) 0.5 wt % DVB and ( $\circ$ ) 1.3 wt % DVB.

use the  $K_p$ - $V$  data of Fig. 2(b) to obtain the individual particle bulk modulus. Remarkably, after doing this, the suspension data of Fig. 1 scales onto a single curve, as shown in Fig. 3, and confirming our hypothesis. Furthermore, the normalized  $\Pi$  and  $K$  remain constant for generalized volume fractions where particle deformation is expected, reflecting that the compression of the suspension is determined by the individual bulk modulus of the particles. As a result,  $K_p$  sets the relevant elastic scale and the  $\zeta$  behavior for the suspension at these high  $\zeta$ . We also note that  $\Pi/K_p \approx 1$  when  $\zeta \approx 1$  and not at smaller  $\zeta$ . This indicates that the osmotic pressure exerted by the microgel suspension on each individual microgel is only comparable to the bulk modulus of the particle around a packing fraction that requires the microgels to be physically in contact with each other. As a result, particle deswelling cannot

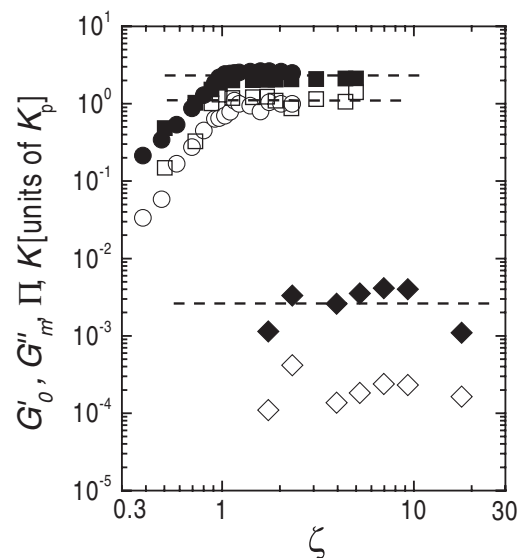


FIG. 3. Bulk modulus ( $\blacksquare, \bullet$ ), osmotic pressure ( $\square, \circ$ ), plateau shear modulus ( $\blacklozenge$ ), and  $G''_m$  ( $\diamond$ ), normalized by the bulk modulus of individual microgels, vs  $\zeta$ . ( $\blacksquare, \bullet$ ) 0.5 wt % DVB, ( $\bullet, \circ$ ;  $\blacklozenge, \diamond$ ) 1.3 wt % DVB.

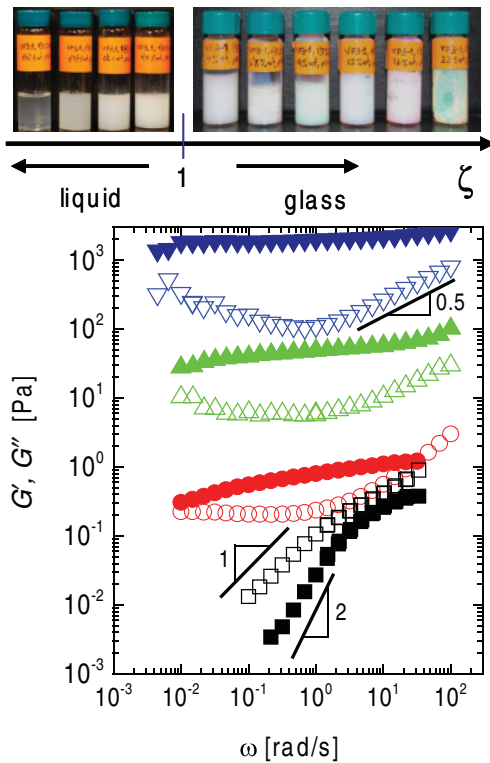


FIG. 4. (Color online) Elastic (solid symbols) and viscous (open symbols) moduli as a function of angular frequency for microgel suspensions with (■, □)  $\zeta = 0.75$ , (●, ○)  $\zeta = 0.99$ , (▲, ▽)  $\zeta = 2.32$ , (▼, ▽)  $\zeta = 9.3$ . The images at the top are samples with  $\zeta$  above and below 1. The absence of Bragg reflections indicates that the solidlike behavior of the samples for  $\zeta > 1$  corresponds to formation of a disordered arrested state.

take place for our microgel suspensions for lower  $\zeta$ , consistent with recent observations [20].

To further characterize the mechanical properties of our microgel suspensions, we perform oscillatory rheology in the linear regime and determine the viscous and elastic moduli  $G'$  and  $G''$  as a function of frequency  $\omega$  for different  $\zeta$ . At low  $\zeta$ , the suspension exhibits the terminal behavior expected for a Maxwell fluid:  $G''(\omega) \sim \omega$  and  $G'(\omega) \sim \omega^2$ , with  $G'' > G'$  [21]. By contrast, for  $\zeta \geq 1$ ,  $G'$  develops a plateau and is larger than  $G''$ , as shown in Fig. 4. This reflects a transition from liquidlike to solidlike behavior at  $\zeta \approx 1$ . Consistent with this, the suspension also develops a yield stress for  $\zeta \gtrsim 1$ . In addition, visual inspection of the samples reveal a lack of Bragg reflections and thus of crystal formation, consistent with what is observed for other microgel suspensions [12,20,22]. Instead, the samples are optically isotropic, as shown by the images in Fig. 4. For  $\zeta > 1$ , the system is thus a disordered, elastic solid. Remarkably, at high frequencies,  $G''(\omega) \sim \omega^{1/2}$ , which is a hallmark exhibited by a variety of systems above the jamming transition [23–28].

We quantify the resistance to shear of our suspensions with the plateau shear modulus  $G'_0$ , which we define as  $G'(\omega = 1 \text{ rad s}^{-1})$ , and with the value of the viscous modulus at the minimum  $G''_m$ , which is a measure of the structural relaxation of the suspension [3]. Remarkably, when normalized by  $K_p$ , both  $G'_0$  and  $G''_m$  remain constant with  $\zeta$ , as shown in Fig. 3.

This emphasizes once more the crucial role played by the single-particle bulk modulus, which not only determines  $\Pi$  and  $K$ , but also  $G'_0$ , further emphasizing that the degree of particle compression determines the interparticle forces, which ultimately determine the shear modulus of the suspension. This is analogous to how the normal force determines solid-solid friction through the friction coefficient, but very different to what sets up the relevant elastic scale in emulsions and foams. In these systems, what matters is the storage of energy at the interfaces separating neighboring drops or bubbles. These facets can be thought of as anharmonic springs, whose compression is related to the deformation of the particles [7]. For our compressible microgel particles, it is the state of compression of the particle what determines the resulting elastic scale of the suspension. Only in a very narrow range in  $\zeta$ , at most above random close packing and below 1, is the behavior of emulsions and microgel suspensions analogous, provided the Laplace pressure in the former is replaced by a contact modulus dependent on the particle Young's modulus [11]. For larger  $\zeta$ , where the microgels must shrink, this analogy breaks down [13,14].

Remarkably, we find that  $K$  is almost three orders of magnitude larger than  $G'_0$  and that the ratio between them remains up to the highest  $\zeta$  we probe, spanning more than an order of magnitude in  $\zeta$ . This is in stark contrast to emulsions and foams, where this difference is approximately an order of magnitude [3,5,6], except for  $\phi \gtrsim 0.85$ , with  $\Pi \rightarrow \infty$  as  $\phi \rightarrow 1$  while  $G'_0$  remains finite. Since for our compressed microgel suspensions this difference is maintained for a much larger concentration range within which  $K$  and  $G'_0$  exhibit the same  $\zeta$  dependence, the small  $G'_0/K$  ratio we observe cannot be related to a divergence in  $\Pi$ . Instead, our results suggest that the origin of this behavior is the intrinsic elasticity of these suspensions. The large difference between the shear and the bulk modulus of our suspensions could be related to an inhomogeneous localization of the strain within our particles, with regions that are much more compressed than others. Depending on whether the suspension is sheared or compressed, both the shape and number of these regions could vary, resulting in a different response to either deformation. However, detailed theoretical calculations are required to address the large difference we observe between  $K$  and  $G'_0$ .

We have shown that both the bulk and shear moduli of compressed microgel suspensions are controlled by the bulk modulus of individual microgel particles, in contrast to compressed emulsions and foams, whose elasticity arises from the interfacial energy stored in the interfaces formed between neighboring drops or bubbles. This markedly different origin can result in a dramatic difference between the shear and the bulk moduli of these suspensions, which in our experiments is as large as three orders of magnitude. This is significantly larger than the corresponding ratio for most materials. Our results emphasize the relevance of being made of compressible building blocks, which can give rise to materials with an unusually large difference in their response to shear and compression.

We thank NSF through the GaTech MRSEC (DMR-0820382).

- [1] M. de Podesta, *Understanding the Properties of Matter* (Taylor & Francis, New York, 2002).
- [2] A. Bedford and W. Fowler, *Engineering Mechanics* (Prentice Hall, New York, 2007).
- [3] T. G. Mason, J. Bibette, and D. A. Weitz, *Phys. Rev. Lett.* **75**, 2051 (1995).
- [4] T. G. Mason, J. Bibette, and D. A. Weitz, *J. Colloid Interface Sci.* **179**, 439 (1996).
- [5] R. Hohler, Y. Y. C. Sang, E. Lorenceau, and S. Cohen-Addad, *Langmuir* **24**, 418 (2008).
- [6] S. Marze, M. Guillermic, and A. Saint-Jalmes, *Soft Matter* **5**, 1937 (2009).
- [7] Martin-D. Lacasse, G. S. Grest, D. Levine, T. G. Mason, and D. A. Weitz, *Phys. Rev. Lett.* **76**, 3448 (1996).
- [8] H. M. Princen, *Langmuir* **2**, 519 (1986).
- [9] H. M. Princen and A. D. Kiss, *Langmuir* **3**, 36 (1987).
- [10] M. Guo and H. M. Wyss, *Macromol. Mater. Eng.* **296**, 223 (2011).
- [11] J. R. Seth, M. Cloitre, and R. T. Bonnecaze, *J. Rheol.* **50**, 353 (2006).
- [12] M. Cloitre, R. Borrega, F. Monti, and L. Leibler, *Phys. Rev. Lett.* **90**, 068303 (2003).
- [13] M. Cloitre, R. Borrega, F. Monti, and L. Leibler, *C. R. Phys.* **4**, 221 (2003).
- [14] S. Adams, W. J. Frith, and J. R. Stokes, *J. Rheol.* **48**, 1195 (2004).
- [15] H. Senff and W. Richtering, *Colloid Polym. Sci.* **278**, 830 (2000).
- [16] A. Loxley and B. Vincent, *Colloid Polym. Sci.* **275**, 1108 (1997).
- [17] H. Senff and W. Richtering, *J. Chem. Phys.* **111**, 1705 (1999).
- [18] B. Sierra-Martín, J. A. Frederick, Y. Laporte, G. Markou, J. J. Liétor-Santos, and A. Fernández-Nieves, *Colloid Polym. Sci.* **289**, 721 (2011).
- [19] S. P. Obukhov, M. Rubinstein, and R. H. Colby, *Macromolecules* **27**, 3191 (1994).
- [20] K. N. Nordstrom, E. Verneuil, P. E. Arratia, A. Basu, Z. Zhang, A. G. Yodh, J. P. Gollub, and D. J. Durian, *Phys. Rev. Lett.* **105**, 175701 (2010).
- [21] R. G. Larson, *The Structure and Rheology of Complex Fluids* (Oxford University Press, New York, 1999).
- [22] D. A. Sessoms, I. Bischofberger, L. Cipelletti, and V. Trappe, *Philos. Trans. R. Soc., A* **367**, 5013 (2009).
- [23] A. J. Liu, S. Ramaswamy, T. G. Mason, H. Gang, and D. A. Weitz, *Phys. Rev. Lett.* **76**, 3017 (1996).
- [24] A. D. Gopal and D. J. Durian, *Phys. Rev. Lett.* **91**, 188303 (2003).
- [25] S. Cohen-Addad, H. Hoballah, and R. Hohler, *Phys. Rev. E* **57**, 6897 (1998).
- [26] B. P. Tighe, *Phys. Rev. Lett.* **107**, 158303 (2011).
- [27] J. J. Crassous, R. Regisser, M. Ballauf, and N. Willenbach, *J. Rheol.* **49**, 851 (2005).
- [28] M. Cloitre, in *Microgel Suspensions: Fundamentals and Applications*, edited by A. Fernandez-Nieves, H. M. Wyss, J. Mattsson, and D. A. Weitz (Wiley-VCH, Berlin, 2011), Chap. 11, pp. 285–309.