Relationship between rheology and structure of interpenetrating, deforming and compressing microgels

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Thermosensitive microgels are widely studied hybrid systems combining properties of polymers and colloidal particles in a unique way. Due to their complex morphology, their interactions and packing, and consequentially the viscoelasticity of suspensions made from microgels, are still not fully understood, in particular under dense packing conditions. Here we study the frequency-dependent linear viscoelastic properties of dense suspensions of micron sized soft particles in conjunction with an analysis of the local particle structure and morphology based on superresolution microscopy. By identifying the dominating mechanisms that control the elastic and dissipative response, we can explain the rheology of these widely studied soft particle assemblies from the onset of elasticity deep into the overpacked regime. Interestingly, our results suggest that the friction between the microgels is reduced due to lubrication mediated by the polymer brush-like corona before the onset of interpenetration.
S oft polymer microgels are fascinating systems whose peculiar properties have resulted in highly diversified applications, spanning from purely academic to the industrial domain. Microgels as model soft spheres have been instrumental in shedding light on fundamental problems relating to phase transitions and microgel additives as rheological modifiers are ubiquitous in consumer and personal care products as well as other industries and applications. The complex nanoscale architecture and softness sets them apart from more conventional solid particles, emulsion droplets or foam bubbles, with profound consequences for the mechanical properties of dense microgel suspensions, which reveal rich and complex features in their concentration dependence. The rheology of hard spherical particles in suspensions is controlled by the volume fraction \( \zeta \) of the dispersed phase as the sole parameter determining a suspension’s phase behavior. In a disordered suspension of hard spheres the maximal volume fraction is reached at random close packing or jamming, \( \zeta_{cp} \approx \zeta \approx 0.64 \). Emulsions, bubbles, and other soft building blocks, on the other hand, can deform, allowing \( \zeta < 1 \). In this range the particles form flat facets at contact points, which in turn store elastic energy, resulting in familiar soft pastes such as mayonnaise or shaving foam. Polymer microgels however are different. They are highly swollen in good solvent conditions, and as a consequence, microgels are compressible in addition to being deformable and therefore highly overpacked states can be reached. Moreover, microgels prepared following standard protocols have a fuzzy polymer shell decorating their compressible cores, allowing for shell compression and interpenetration. Much work has been devoted to the characterization of the elasticity and flow of dense microgel suspensions (or pastes) and common features for microgels of different sizes and softness have been established. The elastic modulus grows rapidly after the liquid–solid transition and then much more slowly at higher concentrations. Relatively little is known, however, about dissipative losses in dense microgel suspensions under shear and their relationship to the microstructure.

Although models and detailed numerical studies have shed much light on microgel rheological properties, there still exists no widely accepted framework that encompasses the entire range of packing densities, from the glassy dynamics and jamming to highly compressed states. Depending on the type (more or less ionic) and size of microgel, osmotic deswelling and interpenetration can be important, but if and when this plays a role has been debated. In the past, little or no in situ information on the single-particle nanoscale level has been available. Recently, however, significant progress has been reported in studies revealing single-particle properties in dense suspensions based on zero average contrast small angle neutron scattering and microscopy.

In this work, we propose a framework to explain the frequency-dependent linear viscoelasticity of microgel suspensions, composed of micron-sized poly(N-isopropylacrylamide) (pNIPAM) microgels with a dense core and a fuzzy corona, from weakly compressed packings to strongly overpacked states by combining the results from oscillatory shear measurements and nanoscale imaging. To this end we characterize the macroscopic rheological properties of soft particle suspensions at a constant temperature and take advantage of the advent of microscopic structural information about individual microgels and pairs of microgel particles resolved via dSTORM superresolution microscopy. Our aim is to describe and connect the mechanisms that determine the viscoelastic and in particular the dissipative behavior across the different concentration regimes. From the latter we can derive important information about the lubricated faceted microgel interfaces and the onset of corona interdigitation. We note that we do not address the properties of ionic or weakly cross-linked microgels and microgel pairs with radii of less than 100 nm. As discussed in recent works, small particles appear to behave qualitatively differently and can for example be overpacked up to a factor of ten without a corresponding increase in elastic modulus.

**Results**

**Superresolution microscopy.** We study swollen pNIPAM microgels prepared by free radical precipitation polymerization at a constant temperature \( T = 22 °C \). From static and dynamic light scattering we find the total microgel radius is \( R_{tot} \approx 470 \text{ nm} \) and the radius of the highly cross-linked core is \( R = 380 \text{ nm} \). Details about the synthesis and characterization are included in the methods section (additional data is plotted in the Supplementary Figs. 1 and 2). The same batch of microgels was used in our earlier work, ref. The experimentally accessible mass concentrations of our suspensions, in wt/wt%, can be converted into effective packing fractions \( \zeta = k \times c \) via the voluminosity \( k = 0.08 \), as shown in ref. We estimate the error bar in setting \( \zeta \) to about \( \pm 3\% \), see also ref. We have verified, using small angle light scattering that, on the time scale of the experiment, the samples do not crystallize (see also Supplementary Fig. 3). The structure and morphology of standard, micron-sized pNIPAM microgels and microgel pairs are resolved via single and dual color superresolution microscopy and small angle light scattering, from marginally jammed to deeply overpacked states, as depicted in Figs. 1 and 2 and discussed in detail in our earlier work, see also Supplementary Fig. 3. We have determined the lateral spatial dSTORM resolution to be approximately 30 nm, about an order of magnitude better than conventional widefield light microscopy as shown in Fig. 1. To obtain a faithful contour of each particle and use it for measuring different geometric features we use the Laplacian of Gaussian edge detector in Matlab (MathWorks, Inc., USA) (for details see methods section). Using synthetic data we can estimate the statistical error of the contour line determination to about \( \pm 5 \text{ nm} \) or less. We can identify three consecutive stages of packing. In the first stage, just above solidification (\( \zeta \approx 0.64 \) or \( c \approx 8\% \)), the microgel’s fuzzy corona or brush is compressed as the measured distance between neighboring particles drops below \( d = 2R_{tot} \); see Fig. 2 and Supplementary Figs. 3 and 4. We note that the compression of the fuzzy corona cannot be visualized directly with dSTORM, due to the extremely low polymer density and the associated noisy signal in this region (see also Supplementary Fig. 2). In the following stage, once the dense cores come into contact (\( \zeta \approx 1.1 \)), interpenetration becomes noticeable and the microgels start to significantly deform, which allows denser packing of the particles without change in measured size (see also Supplementary Fig. 5). Intercorpenetration gradually increases as the contacting facets expand. Finally, once interpenetration and deformations have saturated and the volume is homogeneously filled by the polymer gel (\( \zeta \approx 1.9 \)), isotropic compression and a reduction of the microgel size \( \propto \zeta^{-1/3} \), remains the only mechanism that allows further densification.

**Oscillatory shear experiments.** We perform oscillatory shear measurements in the linear regime (strain \( \gamma = 0.1\% \)) at a fixed temperature of \( T = 22 °C \) covering a wide range of \( \zeta \), from the onset of jamming (\( \zeta \approx 0.64 \)) to deeply overpacked, and determine the elastic and loss moduli as a function of frequency, \( G'(\omega) \) and \( G''(\omega) \). Selected examples of frequency-dependent measurements of \( G' \) and \( G'' \) are shown in Fig. 3a covering the \( \zeta \) range from marginally jammed to deeply overpacked. In all cases we find \( G'' \) being nearly frequency independent and greater than \( G' \), indicating solid like behavior. Dissipative losses, however, are

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relatively high and $G'(\omega)$ shows a minimum around $\omega \sim 1 \text{ rad/s}$, typical of emulsions and foams, in addition to microgels\textsuperscript{16,29,47}. With increasing concentration, the minimum becomes progressively less pronounced and finally, with $\zeta = 1.9$, has all but disappeared. To characterize the $\zeta$-dependent elasticity of our microgel suspensions we take the value $G'(\omega)$ at a fixed frequency of $\omega = 1.2 \text{ rad/s}$, Fig. 3b. Below the jamming packing fraction $\zeta_J$ we measure a weak elastic modulus that we can tentatively ascribe to the entropic glass regime, where the onset of elasticity is given by $G_p \sim k_BT/R^3$, the only energy density scale for noninteracting spheres\textsuperscript{48} (in our case $k_BT/R^3 \approx 0.04 \text{ Pa}$), which then crosses over to a regime governed by the jamming elasticity (see also refs. 33,49 and Supplementary Fig. 6). Starting from $\zeta \sim \zeta_J$, when microgel coronas are in direct contact, we find a steep increase of $G'$. Increasing $\zeta$ by a factor two results in a nearly three order of magnitude increase of $G'$. This trend, however, does not continue over the entire range, instead we observe a slow crossover into a different regime where the slope is reduced considerably\textsuperscript{17,25,28,29,50}.

**Elasticity and storage modulus $G'(\omega)$**. In earlier work Senff and Richtering studied neutral pNIPAM microgels chemically similar to ours but of smaller size $R \sim 130 \text{ nm}$ at 20 °C\textsuperscript{20}. In this pioneering study the rapid increase of elasticity after jamming has been described ad-hoc in terms of a soft interaction potential of the form $\psi \sim r^{-n}$\textsuperscript{20,25} resulting in a power law $G' \sim \zeta^m$ with $m = 1 + n/3$. A more physically descriptive, yet still quantitative approach has been proposed by Scheffold et al.\textsuperscript{28} for micron sized microgels, whereby the microgels are modeled as solid cores, of
size $R$, decorated by polymer brushes, of thickness $L_0 \approx R_{\text{tot}} - R$, which mediate their interactions. The net repulsion between brushes at the microgel periphery, derived from the Alexander—de Gennes scaling model for polymer brushes in good solvent conditions, suffices to describe the onset of solid-like behavior. To derive an expression for $G'$, a local spring constant $k$ is defined which is directly related to the interaction potential between two spheres by $k = -\frac{\partial^2 \psi}{\partial r^2}$, and to the elastic modulus as $G' = k/R$. The complete expression for $G'(\zeta, \alpha) \approx kT R^3 (\tau^{9/4} - \tau^{-3/4})$, where $r(\zeta, \alpha) = (1 - \alpha)/(\zeta L)^{-1/3} - \alpha$, modulus a prefactor of order unity, is derived in $28$ where $s$ is the effective average separation between grafting sites and $\alpha$ is the ratio between core and total radius of the particle. By setting $\alpha = 0.84$ and adjusting the prefactor $k_R T a s^3 = 60$ Pa for a best fit we obtain the dotted orange line shown in Fig. 3b. The value of $\alpha = 0.84$ compares well with the static light scattering result $R/R_{\text{tot}} \approx 0.81$ (see Supplementary Fig. 1) and previous studies on similar systems. $28$.

Fig. 3 Oscillatory shear experiments on dense microgel suspensions. a $G'(\omega)$ (full symbols) and $G''(\omega)$ (open symbols) as a function of frequency $\omega$ for different packing fractions, ranging from marginally jammed to deeply overpacked. b $G'(\omega = 1.2 \text{ rad/s})$ as a function of packing fraction $\zeta$ fitted with the Brush model (orange dotted line) at lower $\zeta$ and with a linear function $G' = 17$ kPa $\times (\zeta - \zeta_c)$, dashed line for $\zeta \geq \zeta_c = 0.87$. The shaded area marks the crossover between the regime controlled by corona compression to the one governed by core-core interactions. Inset: Linear representation of the same data. The estimated error in $\zeta$ shown in panel (b) is $\pm 3\%$.

Friction and loss modulus $G''(\omega)$. Next, we consider the energy losses in the system where the influence of the discrete particulate nature of the suspension at high-packing fractions is striking. Over the entire range we find significant dissipative losses, typical for soft glassy materials, but in stark contrast to macroscopic gels which are almost entirely elastic in their stress response. Calvet et al. $34$ found for macroscopic pNIPAM gels $G''/G' \sim 10^{-3}$, typically about two orders of magnitude less than what we observe.

Anomalously large losses are well known for jammed emulsions, despite the fact there are no static friction forces between the emulsion droplets. Liu et al. showed, that the high-dissipative losses observed for emulsions are due to dynamic dissipation in the fluid confined between planes of facets sliding relative to each other. $56$.

Based on the emulsion work and by comparison with the dSTORM data we can now verify the accuracy and the range of validity of this scenario for our microgel system. As discussed before, we described the microgel by a cross-linked core covered by a brush-like corona. At $\zeta > \zeta_c$ the brushes are partially compressed and the restoring forces lead to the rapidly increasing macroscopic shear modulus $G'$, Fig. 3b. It is known that compressed polymer brushes of thickness $L < L_0$ do not interpenetrate and do not show any noticeable friction when sheared slowly against each other, down to concentration ratios of $L_L \sim 0.1 - 0.15$ $37^{-39}$, suggesting that the model developed for emulsions should also apply to microgels, at least over a limited concentration range, before the onset of interpenetration. As a critical test, we fit $G''(\omega) = A(\omega) \omega^\eta$ with adjustable parameters $A$ and $\eta$ roughly over a decade in frequency $\omega \in [10, 100]$ rad/s. Figure 4a shows these fits in a logarithmic representation for each

elastic modulus $G' = 10^4$ Pa, comparable to data reported by Calvet et al. $34$ for macroscopic homogeneous pNIPAM gels of similar composition to ours ($\sim 5$ mol% BIS).

Interestingly, for these very large filling fractions, we find an
choice of $\zeta$. We note that the contribution of the background fluid is small enough that it can be safely neglected over the range of frequencies $\omega \leq 100$ rad/s considered. Up to $\zeta \approx 0.9$ the data are well-described by the $\omega^{0.5}$ scaling predicted for emulsion droplets with no static friction and also the amplitudes $A(\zeta)$ are similar to those reported for emulsions in ref. 56, inset Fig. 4b. Quantitative differences in $A(\zeta)$ between emulsions and microgels can be explained by the fact that disjoining pressure between the droplet interfaces and the compressed brushes of the microgel corona are not exactly the same.

Figure 4b shows the dependence of the power-law fit parameters $A$ and $\rho$ on $\zeta$. Starting at $\zeta \geq \zeta_0$, deviations from the $\omega^{0.5}$ scaling can be clearly observed. For a solid core the corona would be entirely compressed on the core at $\zeta \to 1.08$, but in our case the core and the corona deformation are coupled and the transition is smeared in the range $\zeta \in [0.87, 1.08]$ due to the compressibility of the core. Thus for $\zeta \geq \zeta_0$ chains in the corona are not stretched anymore and the density of the corona and the core gradually approach each other32, as illustrated in Fig. 4c. As a consequence the penalty for the dangling ends of the corona to interdigitate becomes progressively smaller and losses, expressed by the ratio $G''/G' = \tan \delta$, increase over the entire frequency spectrum probed, full symbols in Fig. 4d (see also Supplementary Fig. 6b). In this regime, two-color dSTORM provides key information about this interdigitation process. The open circles in Fig. 4d show the overlap area $\Delta F/F$ extracted from a $\sim 500$ nm thick z-section through the center of adjacent microgel particles37 (see also Supplementary Fig. 5). The overlap increases rapidly from $\zeta = 0.87$ to $\zeta = 1.9$ and saturates above. We also observe a lowering of the high frequency slope, from $G'' \sim \omega^{0.5}$ to $\sim \omega^{0.3}$, dashed lines in Fig. 4b, marking a deviation from the viscous behavior of jammed emulsions where the slope of $0.5$ is maintained36, but in agreement with previous observations on dense microgel suspensions17,27,31. Interestingly, we find that the anomalously large losses, expressed in terms of $\tan \delta = G''/G'$, scale directly with the overlap area $\Delta F/F$ derived from super-resolution microscopy, as shown in Fig. 4d. In particular, both seem to rise together toward a plateau value at large $\zeta$. We stress the fact that for $\zeta \ll \zeta_0$ the situation is entirely different. As long as the corona is not yet fully compressed, the brush–brush interfaces of the touching microgel coronas are lubricated, $G''$ increases slowly and thus the relative viscous losses drop with the modulus: $\tan \delta \propto 1/G'$ as shown by the red dash-dotted line in Fig. 4d.

**Discussion**

Our investigations reveal that the onset of elasticity in the dense microgel suspensions is governed by compression of their fuzzy outer shells while the friction between the microgels is reduced due to lubrication mediated by this polymer brush-like corona. At higher packing fractions, we visually observe deformation, interpenetration and compression and here the elasticity increases linearly with concentration starting at $\zeta_0$, in agreement with the jamming picture of dense assemblies of homogeneous soft spheres. Deep in the jamming regime our microgel particles have lost their core–shell structure as the soft brush-like corona has already been compressed onto the core. Eventually the faceted and interpenetrating polymeric particles fill space homogeneously. Interestingly, in contrast to other recent studies, we find no evidence for spontaneous deswelling due to an ionic
Methods

Microrheology measurement. Oscillatory shear measurements were performed on non-labeled microgels suspended in pure water. We use a commercial rheometer (Anton Paar MCR 502), using a cone–plate geometry (cone radius 25 mm, angle 1°), equipped with a solvent trap to limit evaporation during the measurement. Selected examples of frequency-dependent measurements of $G’$ and $G''$ are shown in the Supplementary Fig. 6. The results are in very good agreement over a broad range of interest. We note however that the results at the highest concentration of MEA at the lowest concentration of 7.3 wt% ($\dot{\gamma} = 0.584$), gave a torque below the sensitivity of the instrument while for pure water we find the torque sufficient to perform a measurement. This indicates a difference in elasticity between the different solvent conditions in lowest range measured. We attribute this to dissolved ions screening the repulsive interaction between the polymer chains at the higher concentration. To overcome this, we applied ionic initiators for synthesis, weakening interactions when microgels are in close proximity. These very weakly doped or glassy samples are however not in the focus of the present study and shall be discussed elsewhere, using more sensitive methods, such as for example dynamic light scattering or diffusing wave spectroscopy. For higher concentrations we use a temperature controlled centrifuge set to $30 \degree C$ rotating at 30,300 rpm, imposing a force of 17,000 g. To tune the packing fraction to reach the desired final concentration $c_f$ determined by weight. Due to the low-surface charge, at high temperatures and especially at higher concentrations, microgels tend to aggregate which can result in visible flocculation. This is reversible and microgels are quickly redispersed when cooled. Due to centrifugation a concentration gradient will develop in the sample. To homogenize it, the final concentrated sample is again heated, mixed via a vortex mixer then cooled. This process is repeated until the sample appears homogeneous, typically after 1–2 cycles.

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dSTORM supersresolved microscopy. The functionalized microgels were dye-labeled using the formation of stable amide bonds following the reaction between the NHS ester and the amine present in the microgels due to the addition of the acrylamide to the polymer acting as a potential amine donor (Scheme 1). The resulting microgels are kept in the fridge at 4 °C. As dyes we use both the fluorophore Alexa Fluor® 647 and CF680R® (Sigma Aldrich). For dSTORM imaging we mix trace amounts of dye-labeled microgel particles in a matrix of unlabeled microgels and suspend the mixture in a 50 mM MEA (mercaptoethylamine, Sigma Aldrich) to improve the blinking for dSTORM imaging. For two-color dSTORM we apply the spectral demixing approach which is free of cross-talk. For two-color dSTORM we apply the spectral demixing approach which is free of cross-talk. For two-color dSTORM imaging we mix trace amounts of dye-labeled microgel particles in a matrix of unlabeled microgels and suspend the mixture in a 50 mM MEA (mercaptoethylamine, Sigma Aldrich) to improve the blinking for dSTORM imaging. For two-color dSTORM we apply the spectral demixing approach which is free of cross-talk. For two-color dSTORM imaging we mix trace amounts of dye-labeled microgel particles in a matrix of unlabeled microgels and suspend the mixture in a 50 mM MEA (mercaptoethylamine, Sigma Aldrich) to improve the blinking for dSTORM imaging. For two-color dSTORM we apply the spectral demixing approach which is free of cross-talk. For two-color dSTORM we apply the spectral demixing approach which is free of cross-talk. For two-color dSTORM imaging we mix trace amounts of dye-labeled microgel particles in a matrix of unlabeled microgels and suspend the mixture in a 50 mM MEA (mercaptoethylamine, Sigma Aldrich) to improve the blinking for dSTORM imaging. For two-color dSTORM we apply the spectral demixing approach which is free of cross-talk. For two-color dSTORM we apply the spectral demixing approach which is free of cross-talk. For two-color dSTORM we apply the spectral demixing approach which is free of cross-talk. For two-color dSTORM we apply the spectral demixing approach which is free of cross-talk.

Preparation of dense microgel suspensions. Dense, jammed samples were obtained by centrifugation of a dilute stock suspension and redilution with pure deionized water (rheology experiments) or 50 mM MEA (mercaptoethylamine, Sigma Aldrich) aqueous solution for dSTORM. MEA is an amino acid that acts as an antioxidant with chemo-sensitizing and radioprotective properties. We have determined the conductivity of a 50 mM MEA aqueous solution at 22 °C to approximately 150 μS cm⁻¹. Starting from a stoichiometrically 0.0365 g), AAPH, is dissolved in 5 g of H₂O prior to addition to the reaction mixture. Initiators for synthesis, weakening interactions when microgels are in close proximity. These very weakly doped or glassy samples are however not in the focus of the present study and shall be discussed elsewhere, using more sensitive methods, such as for example dynamic light scattering or diffusing wave spectroscopy. Finally, we note that for the weakly elastic microgel packings we observed an unphysical small drop of $G’(\omega)$ at high frequencies for data taken at $\dot{\gamma} = 0.78$ (probably due to residual wall slip) and have thus excluded a small number of data points from the fit in Fig. 4a) to avoid bias.

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analysis. The reconstructed 2D images (composed of square pixels of edge size 15 nm) originate from a plane of ~500 nm thickness adjusted to the center of the particle (also Supplementary Fig. 7). This follows from our image reconstruction protocol, where we set a corresponding threshold for the maximum width of the Gaussian fitting the point image. The two-color images shown in Fig. 2 are taken on dye-labeled pairs of particles located directly on the cover slide to make sure that the imaging section intersects the particle at the same height. Images of the segmented image and ordered counterclockwise. We thus obtain a discrete nm) originate from a plane of ~500 nm thickness adjusted to the center of the experimental conditions apply the same procedure as described above to create an image. The contour analysis of the area of a particle and repositioned them with a Gaussian error of 30 nm. Then we more sophisticated methods involve gradients or Laplacians of the image. What characterizes an edge is a sharp change in intensity, making derivatives well suited to capture their locations. We use the Laplacian of Gaussian edge detector in Matlab (MathWorks, Inc., USA), which allows for edges to be selected based on their strength, and not on intensity values. It also produces closed contours without branching, unlike thresholding and other methods based solely on thresholding. The Laplacian of Gaussian edge detection consists of the following steps: first the image is smoothed by convolution with a Gaussian kernel, then the Laplacian (second derivative in 2D) is calculated and finally the zero-crossings are found which correspond to edges. Examples for the image segmentation done with this method, starting from a dSTORM image of a typical round and a more compressed and deformed particle are shown in Supplementary Fig. 8. The two particles also display different intensities (i.e., density of blinking events detected), yet we can see that the overall shapes and sizes are well captured, with a decrease in size and deformations clearly visible for the second example. Nonetheless, the presence of significant roughness of the contour remains an obstacle in characterizing shape deformations. Visual inspection of the original deformed particle image clearly suggest five corners and nearly flat facets and this are the features to isolate by image analysis. In order to smooth the particle contours while maintaining the prominent shape features we need to eliminate small scale shape fluctuations without significantly altering the overall large-scale shape and corners. To this end we use the method of Fourier descriptors [30], which has been used for a variety of applications in different image analysis. By taking the Fourier transform of the contour different spatial frequencies can be separated, then, by appropriate filtering, a smoothed contour can be retrieved and used as a starting point for further analysis. First, coordinates of the points with respect to the particle’s center of mass are extracted from the segmented image and ordered counterclockwise. We thus obtain a discrete curve \( (x_j, y_j) \) with \( j = 1 \ldots N \) where \( N \) is the number of points. Then, the coordinates are transformed into complex numbers as \( z_j = x_j + i y_j \). Now the Fourier descriptors \( Z(\theta) \) are calculated using a discrete Fourier transform:

\[
Z(k) = \frac{1}{N} \sum_{j=1}^{N} e^{-2\pi i k j / N} (k = 0 \ldots N - 1).
\]

All the spatial information pertaining to the original contour is now encoded in the Fourier descriptors and, through an inverse transform, the full contour can be retrieved. The center of mass is used initially simply for centering the boundary around the particle image. An accurate determination of it is otherwise irrelevant since the descriptors inherit translation invariance from Fourier transforms. Since fine details are encoded in higher frequency components, if those are set to 0 before back transforming, noise can be eliminated and the contour smoothed. We are essentially using a low pass filter, as commonly done in signal processing. The truncated inverse transform \( \hat{z}_j \), using only \( N > N_c \) descriptors, is calculated as \( \hat{z}_j = \sum_{k=-N_c/2}^{N_c/2} Z(k) e^{2\pi i k j / N} (j = 0 \ldots N - 1) \). The new contour coordinates are simply obtained as \( x_j = Re(\hat{z}_j) \) and \( y_j = Im(\hat{z}_j) \). In Supplementary Fig. 9, we can see how different choices of number of descriptors influence the resulting contour. Already with \( N = 30 \) we retrieve all the details and roughness of the original contour, indicating that the eliminated descriptors are redundant. At the other extreme, setting \( N \approx 3 \), we lose too much detail. The contour has four soft corners instead of the five, which can be visually identified. With \( N = 6 \) we obtain a very good representation of the features we can see from the image, noise is removed while all corners are still captured. In this work we have used these settings to smooth contours.

Next, we discuss the reproducibility and statistical error of the edge detection procedure. To this end we generate synthetic dSTORM images of a disc radius 430 nm or a similarly sized hexagon (edge length 430 nm). We randomly select points in the area of a particle and reposition them with a Gaussian error of 30 nm. Then we apply the same procedure as described above to create an image. The contour analysis is performed on this image. As shown in Supplementary Fig. 10 the uncertainty in the location of the edge drops rapidly and reaches values of less than ±50 nm for the experimental conditions \( N \geq 10,000 \) points. Additional systematic errors arise from the tradeoffs already described before such as the low-density tail, Supplementary Fig. 2, and smoothness/ geometrical accuracy, Supplementary Fig. 9. The latter will lead to some smearing of sharp edges which can also be seen in the synthetic data, the edge shape is also shown in Supplementary Fig. 10. From this we can estimate an imaging error of about ±10 nm at the tip of edges. The accuracy of determining the contact lines and the overlap areas shown in Fig. 2 is little affected by this as long as the base resolution is smaller than the edge length, which is the case for dSTORM (but not for standard microscopy). In summary we estimate the reproducibility of the edge detection method in the most relevant regime of overlap for the perturbed particle radius.

Data availability

The data sets generated during and/or analyzed during the current study are available from the corresponding author on reasonable request.

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Author contributions
F.S. and G.M.C. conceived the study. F.S. supervised the study. G.M.C. did all of the rheometry experiments. The dSTORM experiments were carried out by G.M.C. and P.A. C.Z. contributed to the particle size characterization, the Zeta-potential measurements and the image analysis. J.L.H. contributed to the data interpretation. All authors contributed to the data analysis and writing of the paper.

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