

Dense Packing and Symmetry in Small Clusters of Microspheres

Supporting Material

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Materials and Methods

Dispersion preparation Polystyrene particles were prepared by a seeded-growth, emulsifier-free emulsion polymerization (*SI*) with styrene (99%, vacuum distilled) as monomer, ammonium persulfate (98+%, recrystallized) as initiator, and divinyl benzene (80%) as crosslinker. 1.0 mole% crosslinker (relative to monomer) was used in the first stage and 5.0% in the second. After the second stage the particles were mildly aggregated, but could be dispersed by washing in deionized water and sonicating for two minutes in an ultrasonic bath. The particles were transferred to toluene by centrifugation-redispersion in deionized water (twice), ethanol (99%, twice), and toluene (99.5%, twice). The dispersion used to make the sample in Fig. 1B contained about 3% w/w polymer in toluene.

We used the two-stage polymerization process in order to make large particles that we could easily resolve under the optical microscope. In fact, it was possible to make equivalent clusters using the smaller polymer particles that were generated after only a single stage. We also tried to use commercially available crosslinked polystyrene particles, but we found that some of these deformed substantially after they were transferred to toluene, possibly because they contained large amounts of uncrosslinked polymer. Particles prepared according to the procedure above did not have this problem.

Cluster formation 3 ml of the dispersion were added to a mixture of 1% w/w Pluronic F108 surfactant (BASF) in 17 ml deionized water. Toluene is immiscible with water, so the dispersion forms a separate phase that floats on top of the surfactant/water solution. To make an emulsion like that of Fig. 1B, we sheared the two-phase system with a homogenizer (IKA model T25) for 60 seconds at 8000

rpm and 20 seconds at 9500 rpm. The Pluronic surfactant prevents the resulting droplets from coalescing. After homogenization, the emulsion was diluted with 100 ml deionized water and distilled at atmospheric pressure until the boiling point reached 100 °C, at which point all the toluene had evaporated. Equivalent clusters could be produced by adding a water-insoluble supernatant, such as dodecane, to leach toluene from the droplets. We used this slower, more controlled method when observing cluster formation.

It is possible to make a more highly concentrated suspension of clusters simply by adding more dispersion to the water before homogenizing. The amounts of dispersion and water we list above were chosen for convenience only. It is also possible to change the distribution of cluster sizes (to maximize the relative amount of a certain configuration, for example) by varying either the homogenization speed, which affects the droplet size distribution, or the bulk concentration of particles in the toluene dispersion.

Density gradient centrifugation A ‘two-jar’ type gradient maker (Aldrich) was used to prepare a 3-9% w/w linear gradient of Ficoll 400 (Pharmacia) in a 1% w/w Pluronic F108/water solution. 0.5 ml of the cluster suspension were carefully loaded on top of 12 ml of gradient before centrifuging (with a swinging-bucket rotor) for 20 minutes at 4000*g* and 20 °C. A syringe with pipetting needle was used to pull out individual bands from the sample. The fractions were purified by several centrifugation-redispersion cycles in deionized water.

Microscopy and image manipulations To ascertain the configurations of the clusters, we examined samples in the dispersed state with an optical microscope (Nikon) equipped with an oil-immersion objective and Nomarski differential interference contrast. Still images (Figs. 1A, B, C) were captured with a high-resolution digital camera (Nikon), and movies (Fig. 1D) with a video-rate CCD camera (NEC). These images were post-processed to optimize brightness and contrast for print. The time series shown in Fig. 1D is a composite of 13 separate micrographs, with the gray background between images digitally blended to remove seams. Only the even fields of the interlaced video are shown, with the odd fields interpolated.

Clusters in the dried state were imaged with a field-emission scanning electron microscope (JEOL 6300F) after sputter coating with gold. To dry the samples we placed a drop of dispersion on an aluminum sample stub and let the water evaporate. Electron micrographs were also digitally post-processed to optimize brightness and contrast for print.

Light scattering Samples for light scattering were prepared by diluting fractions from the density gradient separation process with pure deionized water in order

to obtain singly-scattering suspensions. A fiber-optic light scattering instrument (Scitech, Inc. model ST100) was used to obtain the scattered intensity as a function of angle at 488 nm and 25 °C. At each angle the scattered intensity was normalized to that of the transmitted beam in order to correct for fluctuations in laser power. The uncertainty in the intensity measurements, as determined by the standard deviation in the count rates, is less than 10% for the smallest and largest angles ($\theta < 10^\circ$ and $\theta > 170^\circ$) and less than 1% for all other data points.

Theoretical scattering curves were calculated in the following manner: First, the diameter of the spheres was determined by fitting the scattered intensity for the first cluster fraction (single spheres) to the form factor predicted by Mie theory, assuming an index of refraction of 1.59 for the particles. We then used the calculated diameter and the observed configurations of spheres in the clusters as inputs to a T-Matrix solver (*S2*), used to calculate the scattering from dilute, randomly-oriented sphere doublets, triangles, and tetrahedra. Other than a simple scaling prefactor, the scattering curves for the clusters have no adjustable parameters.

To calculate the polydispersity of the spheres, we fit the scattered intensity for the first cluster fraction to the Mie form factor integrated over a Gaussian distribution of particle sizes.

References

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