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High-resolution of particle contacts via fluorophore exclusion in deep-imaging of jammed colloidal packings

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HIGHLIGHTS

- New experimental technique for resolving space to detect contacts.
- Experimental measurements of force distribution, soft modes, and critical exponents.
- Finding fragile contacts in random sphere packing.

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ABSTRACT

Understanding the structural properties of random packings of jammed colloids requires an unprecedented high-resolution determination of the contact network providing mechanical stability to the packing. Here, we address the determination of the contact network by a novel strategy based on fluorophore signal exclusion of quantum dot nanoparticles from the contact points. We use fluorescence labeling schemes on particles inspired by biology and biointerface science in conjunction with fluorophore exclusion at the contact region. The method provides high-resolution contact network data that allows us to measure structural properties of the colloidal packing near marginal stability. We determine scaling laws of force distributions, soft modes, correlation functions, coordination number and free volume that define the universality class of jammed colloidal packings and can be compared with theoretical predictions. The contact detection method opens up further experimental testing at the interface of jamming and glass physics.

1. Introduction

The problem with the experimental investigation of jammed colloidal systems [1–3] is that it is difficult to look inside of a particulate packing. This is especially problematic from a theoretical standpoint. While recent theoretical advances have provided a fresh perspective on the long-standing packing problem – including replica theory from spin glasses, constraint satisfaction problems, geometrical and force ensembles – most of these theories are built from the bottom up [4–13]. Therefore, experimentally testing these theories requires full information of the contact network at sufficiently

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Table 1
N is the number of particles whose centers are inside the field of view, average coordination number $\bar{z}$, packing density ϕ, scaling exponent θ' of the weak force distribution, scaling exponent γ of the small gap distribution, and scaling relation $\gamma > 1/(2+\theta')$ [11] for the three packings A, B and C.

Packing	N	$\bar{z}$	ϕ	θ'	γ	$1/(2+\theta')$ [11]
A	1393	7.57	0.66(8)	0.110(5)	0.42(2)	0.474(1)
B	1263	6.79	0.62(4)	0.143(4)	0.62(2)	0.467(1)
C	1486	6.64	0.64(7)	0.170(6)	0.75(3)	0.461(1)

high resolution for resolving fragile contacts at the state of marginal stability observed during the jamming transition. Theoretical predictions of observables like coordination number (number of contacting particles), the scaling of the small-force distribution and geometrical order parameters require exact determination of contact between any two particles. While methods, like X-ray tomography, help analyze contacts between large grains [14,15] (having diameter sizes on the order of mm) these methods are not as effective for studying jammed matter on colloidal length scales. Resolution is limited even in deep imaging of dense jammed colloids [16] and jammed emulsions [17–21] using confocal microscopy. Better resolution is needed if one seeks to determine whether two colloidal particles are in contact at a fragile state of marginal stability near the jamming transition. Here we use the fluorophore signal exclusion of quantum dot nanoparticles at the contact points to determine the contact network with higher resolution [22].

2. Experimental methods

2.1. Sample preparation

We consider a colloidal system of green fluorescent (em: 515–555 nm) silica microspheres in an aqueous-glycerol solution containing red fluorescent (em: 600–700 nm) quantum dot (QD) nanoparticles. The green fluorescence on the surface of the microspheres comes from AlexaFluor® 488 (AF) manufactured by Life Technologies, Inc. This fluorescent dye is attached to surface of silica microspheres using amine and N-hydroxysuccinimide (NHS) ester reaction chemistry [23]. First Bis(succinimidyl) nona(ethylene glycol), manufactured by ThermoFisher Scientific, Inc. is conjugated onto the surface of 5.06 ± 0.44 μm SiO_2-NH_2 microspheres, manufactured by Bang Laboratories. The same chemistry then attaches 8-Arm polyethylene glycol (PEG) amine-terminated star-polymer (MW = 20kDa), manufactured by Nanocs, Inc. and finally attaches AlexaFluor® 488 NHS Ester, (AF; emission: 515–555 nm) to the PEG amine groups positioned on the microsphere surface. This surface chemistry is necessary for uniform fluorescence that is devoid of dark patches upon the surface of each particle. The added PEG also produces short-range steric repulsive interactions [24] that largely negates adhesive forces and minimizes friction between particles [25]. This allows particles to move freely and to pack randomly in aqueous-glycerol solution.

The size and density of the fluorescent silica particles causes gravitational settling to exceed Brownian motion (i.e., Péclet number ~ 329). Hence, the particles pack naturally by sedimentation. Therefore, the "pressure" in each packing equals the weight of the particles themselves. Centrifugation momentarily adds to the weight or pressure of each packing to insure compaction. No centrifugation was used on packing A listed in Table 1. Packings B and C were each centrifuged at $2210\times g$ and $4416\times g$, respectively, using an Eppendorf centrifuge (model 5804R).

Quantum dot (QD) nanoparticles manufactured by Thermo Fisher Scientific, Inc. (cylindrically shaped and approximately 8×15 nm in size [26] with a narrow red emission peak at 600–700 nm) are added to the aqueous-glycerol solution of the compacted particulate system. The refractive index of the solution is carefully designed to match the refractive index of the particles which allows for deep-imaging into the packing using confocal microscopy. Fig. 1b–c show two 3D confocal images of green and red fluorescence from the *same* packing acquired *at the same time* using different fluorescent channels.

2.2. Analysis

The contact detection method probes the exclusion of quantum dot nanoparticles (QDs) from the contact gap between any two neighboring colloidal particles and also monitors the emission of AF at the surface of the particles. Fig. 1a provides a schematic representation of QDs being excluded from the contact gap. The exclusion of QDs is accompanied by a noticeable decrease in fluorescent signal from QDs. This decreasing signal intensity correlates with the size of the inter-particle space from which the QDs are excluded and thus provides a measure of the contact gap [27] in a process that we call *fluorophore signal exclusion*. We note that, technically, we are not measuring the size of QDs as in super-resolution Stimulated-Emission-Depletion (STED) techniques [28,29]. Thus, our detection method does not break the diffraction limit. Instead, we infer information on the contact gap by measuring the fluorescent signal from QDs and correlating it with the gap between particles.

Fig. 2a–c exemplify, for three characteristic cases of contacts, the intensity profile of AF ($I_{\mathrm{AF}}^{\mathrm{c-c}}$) along a line c-c between the centers of nearest neighboring particles and the intensity profile of QDs ($I_{\mathrm{QD}}^{\perp}$) along a line p-p that is perpendicular to the line c-c as sketched in Fig. 2a, left panel.

Fig. 2a shows the case of well-separated particles. In this case, two adjacent peaks in $I_{\mathrm{AF}}^{\mathrm{c-c}}$ locate the edges of neighboring particles (the green rings of AF). These peaks represent the bounding edges of the inter-particle space or the contact gap.