Supplementary Information: Longitudinal Eigenvibration of Multilayer Colloidal Crystals and the Effect of Nanoscale Contact Bridges

SAMPLE FABRICATION

The aluminum-coated soda lime glass substrates were cleaned by soaking in isopropanol and acetone for ten minutes each, and then rinsed with deionized (DI) water and dried under nitrogen flow. Following this, the substrates were coated with a 20-nm-thick silica layer via chemical vapor deposition. The colloidal suspensions for these samples were purified by centrifuging the suspension at 4000 rpm, discarding the supernatant and redispersing the particles in DI water or ethanol. This purification procedure was repeated three times for all samples, except in the case of Sample 2, where the colloidal suspension was centrifuged once. Details of the self-assembly parameters and the layer thicknesses characterized for the multilayer samples in this study are listed in Table S1. The samples with the microsphere suspension in water were left to dry in an oven at 75° C, while the samples immersed in the ethanol suspension were placed under a plastic container to avoid external airflows and left to dry under ambient laboratory conditions.

TABLE S1: Details of sample fabrication parameters for the multilayer samples.

Sample	Concentration (% v/v)	Solvent	Drying Environment	Centrifuged	Layer Thicknesses Characterized	Monolayer Resonance Detected
1	0.2	Ethanol	Ambient	3x	1, 2, 3, 4, 5, 7, 8, 12	Yes
2	0.01	DI Water	Oven, 75° C	1x	1, 2, 3, 4, 5, 9, 12	Yes
3	1	Ethanol	Ambient	3x	6, 7	No
4	0.5	Ethanol	Ambient	3x	2, 3, 4, 5, 6, 7, 8, 9	No
5	0.3	Ethanol	Ambient	3x	2, 3, 4, 5, 6, 7, 9	No
6	0.01	DI Water	Oven, 75° C	3x	2, 3, 4	No
7	0.01	DI Water	Oven, 75° C	3x	2, 3, 4, 5, 6	No

LASER ULTRASONIC SETUP DETAILS

For the measurements on Sample 2, the pump beam was focused to an elliptical spot (436 μm x 76 μm at the $1/e^2$ intensity level), whereas for all the other samples, the pump beam was focused to a 200 μm diameter circular spot. The interferometric signals were averaged over 10^4 pump pulses for all samples, except in the case of the measurements on the monolayer, five-, seven-, eight- and twelve-layer regions of Sample 1, which were averaged over 10^6 pump pulses to achieve an improved signal-to-noise ratio.

SIGNAL PROCESSING PROCEDURE

Time-resolved signals were recorded at a positive and negative phase setting by varying the optical path difference between the probe and the reference beams via a rotating fused silica window placed in the path of the probe beam. The net signal was obtained by subtracting the averaged waveforms collected at positive and negative phase settings. A segment of 0.75 μs of the signal starting from the sharp initial rise (corresponding to the arrival of the pump pulse) was used for further signal processing. This segment of the signal was zero-padded after the oscillations completely decayed below the noise floor, differentiated with respect to time to remove the thermal decay component from the signal, and normalized with respect to its maximum amplitude. A Fast Fourier Transform (FFT) was then applied to the normalized signal.

WORK OF ADHESION AT THE SPHERE-SUBSTRATE AND SPHERE-SPHERE INTERFACES

We estimate the work of adhesion between identical polystyrene microspheres w_{P-P} and that between the polystyrene microspheres and the silica-coated substrate w_{P-S} in terms of the Hamaker constant A, using $w = \frac{A}{12\pi D_0^2}$

($D_0 = 0.165$ nm is a standard value used for the interfacial cutoff separation distance for a variety of media [1]). This coefficient takes into account the van der Waals forces between the two surfaces in contact. The expression for the Hamaker constant A_{131} for two polystyrene surfaces (denoted as medium 1) interacting across medium 3 (air) is:

$$A_{131} = \frac{3kT}{4}\left(\frac{\epsilon_1 - \epsilon_3}{\epsilon_1 + \epsilon_3}\right)^2 + \frac{3h\nu_{e1}}{16\sqrt{2}}\frac{(n_1^2 - n_3^2)^2}{(n_1^2 + n_3^2)^{3/2}} \tag{1}$$

where $T = 293$ K is room temperature, $\nu_{e1} = 2.3 \cdot 10^{15}$ Hz is the main electronic absorption frequency of polystyrene in the UV, k is Boltzmann's constant, h is Planck's constant, $\epsilon_1 = 2.55$ F/m and $\epsilon_3 = 1.0$ F/m are the permittivities of polystyrene and air, respectively, and $n_1 = 1.56$ and $n_3 = 1.00$ are the refractive indices of polystyrene and air, respectively. All of the preceding constants are tabulated in Ref. 1. Using Eq. 1, we calculate $A_{131} = 6.53 \cdot 10^{-20}$ J. This gives a work of adhesion $w_{P-P} = 0.06$ J/m^2 between the polystyrene microspheres.

Similarly, we use Eq. 1 to calculate the Hamaker constant for two silica surfaces (denoted as medium 2) interacting in air (medium 3), with the corresponding material properties of silica: permittivity $\epsilon_2 = 3.8$ F/m, refractive index $n_2 = 1.45$, and electronic absorption frequency in the UV $\nu_{e2} = 3.2 \cdot 10^{15}$ Hz [1]. We obtain $A_{232} = 6.36 \cdot 10^{-20}$ J. We use a combining relation to obtain an approximate value for the Hamaker constant between polystyrene and silica, $A_{132} \approx \sqrt{A_{131}A_{232}}$, such that $A_{132} \approx 6.44 \cdot 10^{-20}$ J. The corresponding work of adhesion between polystyrene and silica is $w_{P-S} = 0.06$ J/m^2.

CALCULATION OF THE EFFECTIVE INTERLAYER CONTACT STIFFNESS USING THE DMT MODEL

The normal contact stiffness between two colloidal particles $G_{N,DMT}$ is derived from the linearized force-displacement curve prescribed by the DMT model [2], and is expressed as, $G_{N,DMT} = \frac{3}{2}(2\pi w_{P-P}R_e^2 E_{P-P}^{*2})^{1/3}$, where w_{P-P} is the work of adhesion between the two polystyrene surfaces, R_e is the effective radius (equal to half the radius of the particle), and E_{P-P}^* is the effective modulus of the contact and is defined in terms of the Young's modulus E_P and the Poisson's ratio ν_P of the particle, $E_{P-P}^* = \frac{2}{3}\frac{E_P}{1-\nu_P^2}$. The effective interlayer normal contact stiffness G_e, DMT is then derived by accounting for the contributions of the three normal $G_{N,DMT}$ and transverse G_S contact springs each in an HCP unit cell along the out-of-plane direction to be $G_{e,DMT} = G_{N,DMT}(2+\nu^*)$, where $\nu^* = \frac{G_S}{G_{N,DMT}} = 2\frac{1-\nu_P}{2-\nu_P}$ is the ratio of the interparticle shear and normal contact stiffnesses [3, 4].

ESTIMATION OF DISPLACEMENT AMPLITUDE IN THE ALUMINUM FILM

We estimate the thermoelastic strain in the aluminum film induced by the pump laser pulse using the relation in reference [5], $\eta_0 = 3\kappa\alpha_L(1 - R)Q/(A_p C\xi_0\rho_0 c_L^2)$, where $\kappa = 67.6$ GPa is the bulk modulus, $\alpha_L = 23.1$ μm/m·K is the linear thermal expansion coefficient, $\rho_0 = 2.7$ g/cm^3 is the density, $C = 2.46$ MJ/m^3, K is the volumetric heat capacity, $R = 0.92$ is the optical intensity reflection coefficient, $\xi_0 = 6.8$ nm is the optical penetration depth, $c_L = 6300$ m/s is the longitudinal wave speed in aluminum [6], A_p is the area of the pump spot, and $Q = 7$ μJ/pulse is the pump pulse energy at the sample. From the thermoelastic strain, we estimate the displacement in the aluminum film to be $u_z = \eta_0\xi_0 = 340$ pm.

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[1] Israelachvili, J.N. *Intermolecular and Surface Forces* (Elsevier, Inc., Burlington, MA, 2011).
[2] Muller, V.M.; Derjaguin, B.V.; Toporov, Y.P. On two methods of calculation of the force of sticking of an elastic sphere to a rigid plane. *Colloids and Surfaces* **1983** 7, 251-259.
[3] Mindlin, R.D. Compliance of elastic bodies in contact. *J. Appl. Mech.* **1949** 16, 259-268.
[4] Merkel, A.; Tournat, V.; Gusev, V.E. Dispersion of elastic waves in three-dimensional noncohesive granular phononic crystals: properties of rotational modes. *Phys. Rev. E* **2010** 82, 031305.
[5] Matsuda, O.; Larciprete, M.C.; Voti, R.L.; Wright, O.B. Fundamentals of picosecond laser ultrasonics. *Ultrasonics* **2015** 56 3-20.
[6] ASM International Handbook Committee, *ASM Handbook, Volume 2 - Properties and Selection: Nonferrous Alloys and Special-Purpose Alloys* (ASM International, Materials Park, OH 1990).