Supplementary Information (SI) for Soft Matter.

Supplementary Information: Theoretical Study of the Impact of Dilute Nanoparticle Additives on the Elasticity of Dense Colloidal Suspensions

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The figures below are all referred to and discussed in the main text. They provide additional results of interest, and also buttress some broader scientific statements and conclusions made in the main text. In all the theoretical plots below, the black square open symbols represent results for the reference one-component hard sphere system.

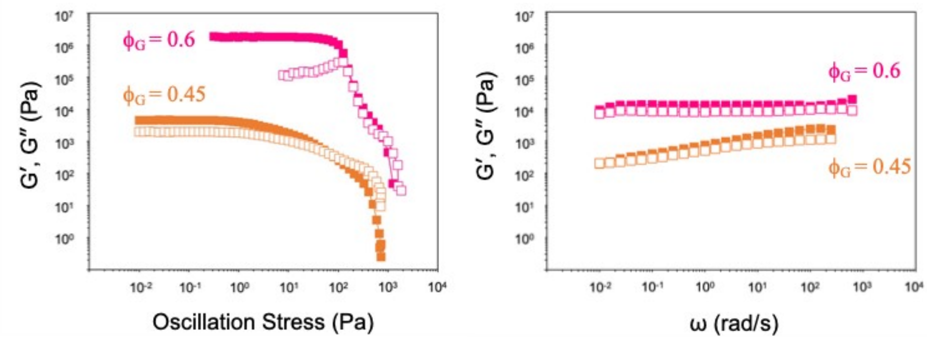

Figure S1: Log-log plots of the measured shear elastic (G') and loss (G'') moduli as a function of shear stress (left) and frequency (ω) (right) for granular-nanoparticle mixtures of varying granular particle packing fraction at a constant nanoparticle loading of 1.5% by volume.

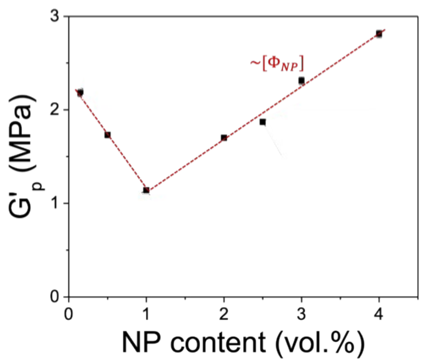

Figure S2: Measured shear elastic modulus (G') as a function of nanoparticle loading for granular-nanoparticle mixtures with a constant granular particle packing fraction of $\phi_G = 0.6$.

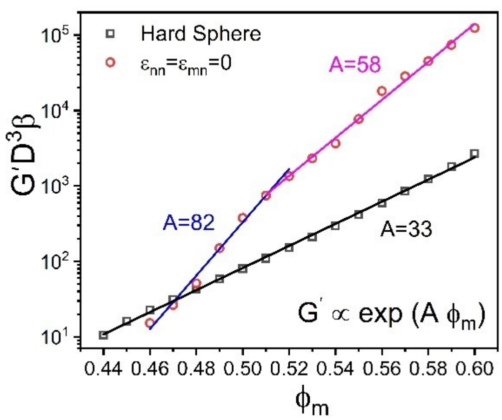

Figure S3: Log-linear plot of the nondimensionalized elastic shear modulus as a function of colloid packing fraction ϕ_m for fixed nanoparticle packing fraction $\phi_n = 0.025$ and size ratio D/d=10. All the interactions between different species are purely hard-core repulsion.

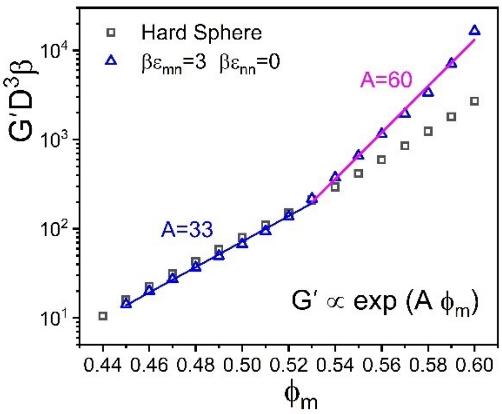

Figure S4: Log-linear plot of the nondimensionalized elastic shear modulus as a function of colloid packing fraction ϕ_m with interfacial attraction between colloids and nanoparticles of contact strength $3k_BT$ and range 0.002D. The NP packing fraction is ϕ_n = 0.025, and the size ratio D/d=10. The other interactions between colloid-colloid and NP-NP are purely hard-core repulsion.

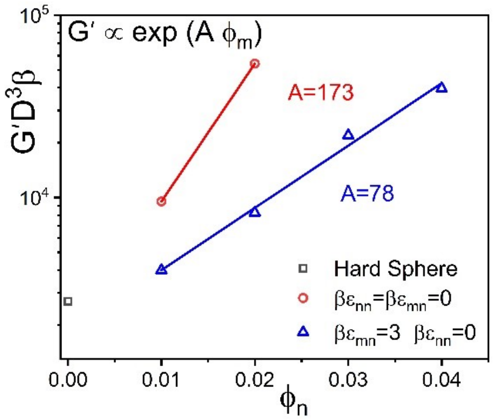

Figure S5: Log-linear plot of the nondimensionalized elastic shear modulus as a function of nanoparticle packing fraction ϕ_n for a mixture with an interfacial attraction between colloids and nanoparticles of contact strength $3k_BT$ and range 0.002D, colloid packing fraction ϕ_m = 0.6, and size ratio D/d=10. The colloid-colloid and NP-NP are purely hard-core repulsion.

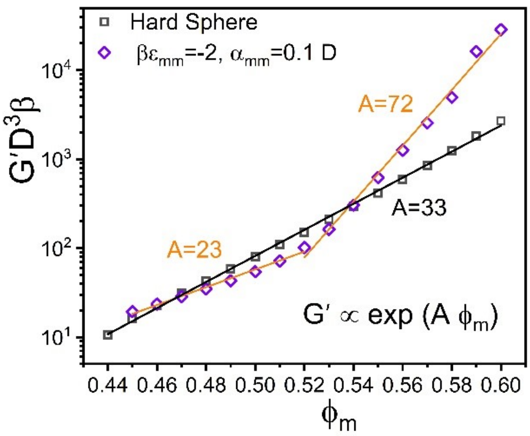

Figure S6: Log-linear plot of the nondimensionalized elastic shear modulus as a function of colloid packing fraction ϕ_m of a mixture with direct repulsions between colloids of strength $-2k_BT$ and range 0.1D, NP packing fraction ϕ_n = 0.025, and size ratio D/d=10. The other interactions between colloid-NP and NP-NP are purely hard-core repulsion. .

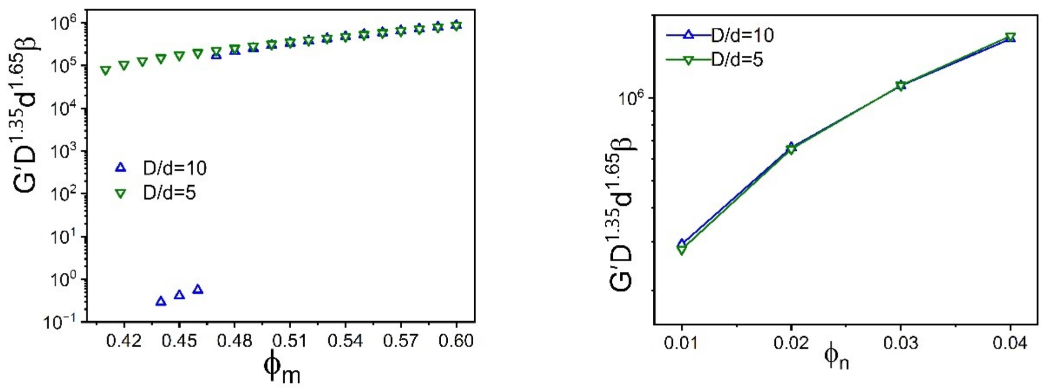

Figure S7: Log-linear plot of the dimensionless elastic shear modulus scaled by the mixed volumetric factor of $D^{1.35}d^{1.65}$ as a function of (a) colloid packing fraction at fixed NP packing fraction 0.025, and (b) nanoparticle volume fraction at fixed colloid packing fraction 0.60, for the colloid-NP interfacial attraction of strength $4k_BT$ and range 0.002D mixture. An excellent collapse is obtained.

Theoretical Calculation of the Shear Modulus of Binary Mixtures

The time-dependent shear modulus is given by the following well known exact expression [1]

$$G(t) \equiv \frac{1}{k_BTV}\langle \sigma^{xy} e^{\Omega t} \sigma^{xy} \rangle \qquad (1)$$

where σ^{xy} is the microscopic stress tensor, and $e^{\Omega t}$ is the time evolution operator. Neglecting hydrodynamic interactions and using a simplified notation

$$\sigma^{xy} = \frac{1}{2} \sum_{\substack{i,j \to 1 \\ i \neq j}}^{N^{total}} R_{ij}^{x} \frac{\partial U_{ij}(R_{ij})}{\partial R_{ij}^{y}} \qquad (2),$$

where the sum is over all particle pairs in the mixture that interact via the pair potential $U_{ij}(r)$ and R_{ij}^{x} is the x component of the displacement vector between particles i and j. A collective bilinear projection operator associated with density fluctuations is then defined as [1]

$$\bar{P}_3 \equiv \frac{1}{2} \frac{V}{(2\pi)^3} \int dk \sum_{\alpha,\beta,\gamma,\delta}^{E} \langle \cdots A^{\beta}(k) A^{\alpha}(-k) \rangle \times S_{\alpha\delta}^{(-1)}(k) S_{\beta\gamma}^{(-1)}(-k) A^{\delta}(k) A^{\gamma}(-k) \qquad (3).$$

where $A^{\alpha}(k) \equiv \left(N_{\alpha}^{\text{total}}\right)^{-1/2} \sum_{l=1}^{N_l^{\text{total}}} e^{-ik \cdot R_j} - \sqrt{N_{\alpha}^{\text{total}}} (2\pi)^3 \; V^{-1} \delta(k)$ and $k = 1,2,....E$. Eqn (1) is then approximated by projection of stress onto the density fluctuation variable:

$$\Delta\eta(t) \cong \frac{1}{k_B T V} \langle \bar{P}_3 \sigma^{xy} e^{\Omega t} \bar{P}_3 \sigma^{xy} \rangle \qquad (4)$$

Well-known algebraic manipulations then yield [1]

$$\Delta\eta(t) = \frac{1}{2k_B T} \frac{1}{(2\pi)^3} \int dk \sum_{\alpha,\beta,\gamma,\delta}^{E} \sum_{\alpha',\beta',\gamma',\delta'}^{E} U_{\alpha\beta}(k) U_{\alpha'\beta'}(k) \times S_{\alpha\delta}^{-1}(k) S_{\alpha'\delta'}^{-1}(k) S_{\beta\gamma}^{-1}(k) S_{\beta'\gamma'}^{-1}(k) S_{\gamma\gamma'}(k,t) S_{\delta\delta'}(k,t) \qquad (5)$$

where

$$U_{\alpha\beta}(k) \equiv \langle \sigma^{xy} A^{\alpha}(k) A^{\beta}(-k) \rangle \qquad (6)$$

Integrating by parts allows Eq. (6) to be expressed as

$$U_{\alpha\beta}(k) = k_B T \frac{1}{2} \sum_{\substack{i,j \to 1 \\ i \neq j}}^{N^{total}} \left\langle \frac{\partial}{\partial R_{ij}^{y}} R_{ij}^{x} A^{\alpha}(k) A^{\beta}(-k) \right\rangle \qquad (7)$$

From Eq. (7) one obtains:

$$U_{\alpha\beta}(k) = k_B T \frac{k_x k_y}{k} \frac{d}{dk} S_{\alpha\beta}(k) \qquad (8)$$

Substituting Eq. (8) into Eq. (5), and using Eqn (A2) of the Appendix of the main text, one obtains the key Eq.(7) of the main text for the dynamical elastic shear modulus in the long time limit $t \to \infty$.

References

[1] G. Nägele and J. Bergenholtz, J. Chem. Phys., 1998, **108**, 9893.