<u>Supplementary document:</u>

Dynamic Modulation of Inter-Particle Correlation during Colloidal Assembly in a Confined Medium: Revealed by Real time SAXS
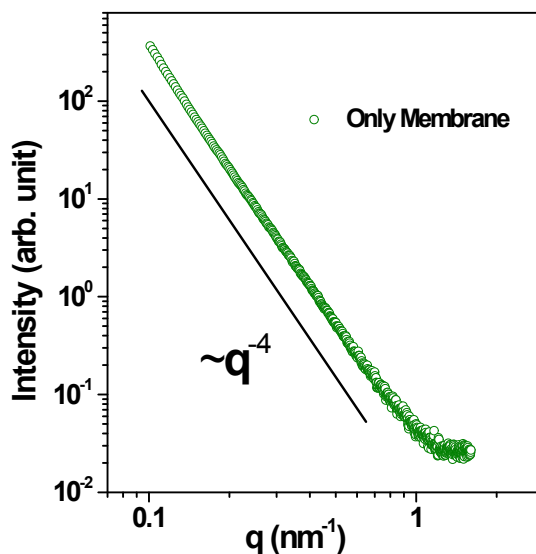
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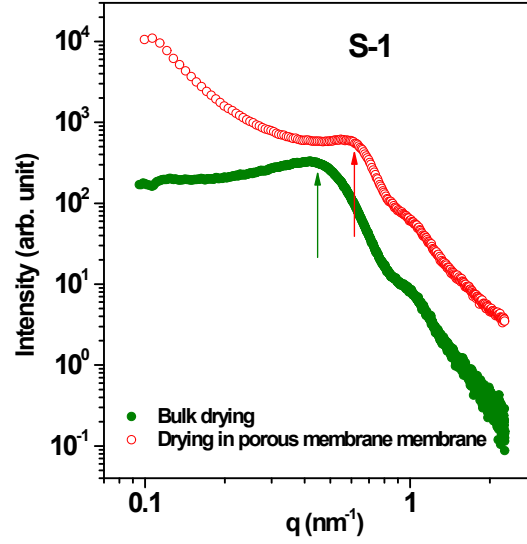
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Fig. SM1: SAXS profile from the GS0.22 membrane. The power law variation of intensity with q is seen.
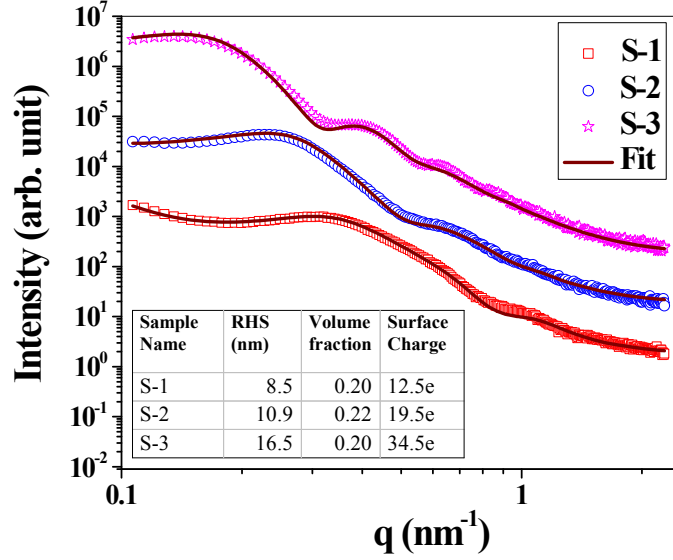
Fig. SM2: *SAXS profile from the assembled particle in membrane and gel sample obtained after bulk drying are significantly different. The position of the peak in SAXS profile is at significantly higher q value in the first case, indicating larger value of local volume fraction than bulk drying.*

The size distribution of the colloids was obtained from scattering measurements on diluted dispersion of the virgin colloids using the following equation

$$I(q) = n_{silica} \Delta\rho^2 \int_0^\infty P(q, R) V^2(R) D(R) dR$$

where P(q,x) is the form factor of a particle with radius x, V(x) is the volume of the particle, n is the number density, $(\Delta\rho)^2$ is the scattering contrast and D(x) represents the size distribution of the particle.

Intensity (arb. unit) vs **q (nm⁻¹)**

Legend: S-1, S-2, S-3, Fit

| Sample Name	RHS (nm)	Volume fraction	Surface Charge
S-1	8.5	0.20	12.5e
S-2	10.9	0.22	19.5e
S-3	16.5	0.20	34.5e

Fig. SM3: Fitting of the scattering profiles (at t=0) considering Hayter-Penfold RMSA model structure factor for charged colloids.

Table: Values of estimated time constant of the processes obtained from fitting the equation

$$\phi(t) = \begin{cases} \phi_0 + A\exp(t/\Delta) & \forall\ t \le t_m \\ a\exp\left(-\dfrac{(t-\tau_1)}{\Delta_1}\right) + \dfrac{b}{1+\exp\left(-(t-\tau_2)/\Delta_2\right)} & \forall\ t > t_m \end{cases}$$

	Δ (min)	τ_1 (min)	τ_2 (min)	Δ_1 (min)	Δ_2 (min)
S-1	27	40	42	4.8	3.9
S-2	30	41	42	4.9	3.9
S-3	34	49	49	5.2	3.9

Δ represents characteristic time that corresponds to the rate of growth in ϕ in the first phase of evaporation. τ_1 and τ_2 represent the characteristic times at which the modulation in f occurs due to two competitive processes, whereas Δ_1 and Δ_2 represent their corresponding rate.
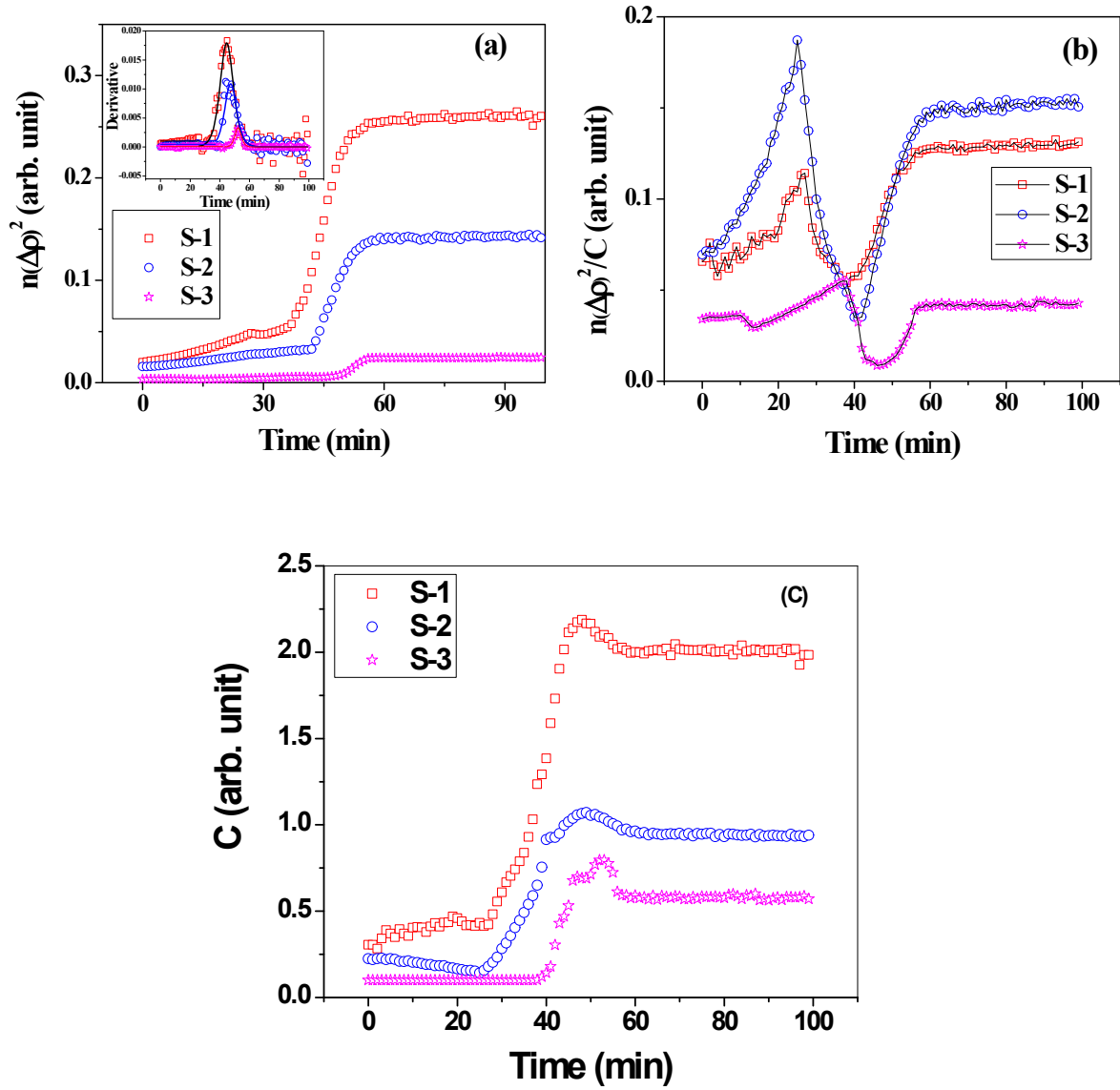
Fig. SM4: Evolution of $n(\Delta\rho)^2$, $n(\Delta\rho)^2/C$ and C with time

To obtain the temporal variation of $n(\Delta\rho)^2$, ϕ and C, the equation (2) has been fitted to all the experimental profiles, by using non-linear least square method. The particle size distribution, as obtained from the scattering profile of dilute colloids, was kept fixed while

fitting the above model to the *in-situ* scattering data. Estimated evolution of $n(\Delta\rho)^2$ and $n(\Delta\rho)^2/C$ is depicted in Fig. SM4.

Fig. SM4 (a), clearly shows that $n(\Delta\rho)^2$ increases with time and ultimately reaches a plateau. It should be noted that 'n' does not change as the total number of silica particles remain constant throughout and thus, such increase is attributed to the increase in scattering contrast with time. The rate of increase in contrast is somewhat sluggish at the initial stage but becomes fairly rapid after a critical time ($t_c \sim 40$ minutes) of evaporation and the rate of increase of passes through a maximum before it reaches plateau (inset of Fig. SM4 (a)). The continuous increase of $n(\Delta\rho)^2$ can be understood by gradual increase of scattering contrast of silica particles. The X-ray (considering CuK_α) scattering length density of silica (ρ_S), cellulose (ρ_{Cel}) and water (ρ_W) is $\sim 1.88 \times 10^{11}$ cm^{-2}, 1.36×10^{11} cm^{-2} and 0.95×10^{11}cm^{-2}, respectively. At time t=0, the contrast of silica particles is primarily with water [$\Delta\rho \sim (1.88-0.95) \times 10^{11}$ cm^{-2}] and at the end the same is with air [$\Delta\rho \sim 1.88 \times 10^{11}$ cm^{-2}]. Thus, the contrast increases with time that leads to gradual increase of $(\Delta\rho)^2$ with time. Thus, $(\Delta\rho)$ for silica at any instant of time may be expressed as $\Delta\rho_S(t) = [\rho_S - f_W(t)\rho_W]$, where $f_w(t)$ is the volume fraction of water retained in the pore of the membrane. It should be noted that the increase in $(\Delta\rho)^2$ is much faster after t_c (~ 40 minutes) preceded by initial sluggish growth. Initially, the bulk water evaporates from the whole membrane. However, at the later stage when the evaporation of the bulk water is complete, the evaporation starts for water layer attached to the surface of the nano-particles. At this stage, the rate of evaporation is much faster due to availability of large specific surface area on individual colloidal particles.

Analyses suggest that the increase of $(\Delta\rho)^2$ beyond t_c can be well represented by a growth of

sigmoidal $\left(U+\dfrac{U-V}{1+e^{-(t-tc)/\Delta t}}\right)$ type while the same at below t_c shows nearly linear behaviour.

Interestingly, the ratio of $n(\Delta\rho)^2$ to C shows a maximum at around 20 min and then passes

through a subsequent minimum t_c before reaching plateau almost after 60 min. It should be noted

that the time corresponding to minimum of $n(\Delta\rho)^2$ /C coincides with the time when the increase-

rate of $n(\Delta\rho)^2$ passes through the maximum. The fall in the ratio $n(\Delta\rho)^2$ /C in the intermediate

stage arises either due to increase in the value of C, or due to increase in low q scattering because

of assembled structure larger than individual silica size.

Classical DFT:

      Spherical particles interacting with the well-known Derjaguin-Landau-Verwey-Overbeek

(DLVO) (screened Coulomb) potential (u(r)) satisfying the linearized Poisson Boltzmann equation

$$\beta u(r) = \gamma \frac{e^{-ks}}{s}, \quad \text{for } r < d \text{ , (when s < 1)}$$
$$= 0 \quad \text{for } r > d \text{ (when s > 1)}$$

where r denotes the inter-particle distance, and $s(=r/d)$ is the scaled distance. In the above equation β

[$=1/(k_BT)$] is the inverse temperature and γ is the Coulomb coupling strength as given by

$$\gamma = \frac{\beta Z^2 e^2}{\varepsilon d(1+k/2)^2} e^k$$

and k ($=\kappa d$) is the inverse screening length.

      As the colloidal suspension is confined in pore, an external potential arises which makes the

system inhomogeneous and thus the classical density functional theory (DFT) of the inhomogeneous

fluids remains as an appropriate theory to handle such systems. According to classical DFT, the grand potential of a many-particle system can be expressed as a functional of inhomogeneous density distribution $\rho(r)$ as

$$\Omega[\rho] = F[\rho] + \int d\mathbf{r}[u_e(\mathbf{r}) - \mu]\rho(\mathbf{r}),$$

where μ is the chemical potential and $u_e(\mathbf{r})$ is the external potential causing the inhomogeneity in the system. The quantity $F[\rho]$ in the above equation is the Helmholtz free energy functional of the inhomogeneous system and it can be further split into ideal free energy $F_{id}[\rho] = \beta^{-1} \int d\mathbf{r}\rho(\mathbf{r})\left\{\ln[\rho(\mathbf{r})\Lambda^3] - 1\right\}$, where Λ represents thermal de-Broglie wavelength and the excess free energy $F_{ex}[\rho]$. The density profile of an inhomogeneous system in equilibrium with a bulk system of homogeneous density ρ_0, can be obtained by minimizing the grand potential and is given by

$$\rho(\mathbf{r}) = \rho_0 \exp[-\beta u(\mathbf{r}) + c^{(1)}(\mathbf{r};[\rho]) - c_0^{(1)}(\rho_0)]$$

where the one-particle direct correlation function (DCF) $c^{(1)}(\mathbf{r};[\rho])$ is the functional derivative of the excess free energy functional $F_{ex}[\rho]$ with respect to inhomogeneous density distribution $\rho(\mathbf{r})$ and $c_0^{(1)}(\rho_0)$ refers to the one-particle DCF of the homogeneous fluid. Using perturbative approach, above equation for the density profile can be written as

$$\rho(\mathbf{r}) = \rho_0 \exp\left\{-\beta u(\mathbf{r}) + \int d\mathbf{r}_2 c_0^{(2)}(|\mathbf{r} - \mathbf{r}_2|;\rho_0)\Delta\rho(\mathbf{r}_2) + \frac{1}{2}\int d\mathbf{r}_2 \int d\mathbf{r}_3 c_0^{(3)}(\mathbf{r},\mathbf{r}_2,\mathbf{r}_3;\rho_0)\Delta\rho(\mathbf{r}_2)\Delta\rho(\mathbf{r}_3)\right\},$$

where $c_0^{(2)}(|\mathbf{r} - \mathbf{r}_2|;\rho_0)$ and $c_0^{(3)}(\mathbf{r},\mathbf{r}_2,\mathbf{r}_3;\rho_0)$ are the two- and three-particle DCF of the homogeneous fluids. Further simplification of the three-particle DCF leads to the form

$$\rho(\mathbf{r}) = \rho_0 \exp\left\{-\beta u(\mathbf{r}) - \gamma d\int d\mathbf{r}_2 \frac{e^{-\kappa|\mathbf{r}-\mathbf{r}_2|}}{|\mathbf{r} - \mathbf{r}_2|}\Delta\rho(\mathbf{r}_2) + \int d\mathbf{r}_2 c_s(|\mathbf{r} - \mathbf{r}_2|/d;\rho_0)\Delta\rho(\mathbf{r}_2) + \int d\mathbf{r}_2 a(|\mathbf{r} - \mathbf{r}_2|)\overline{(\delta\rho(\mathbf{r}_2))^2}\right\}$$

In the above equation $\overline{\delta\rho(\mathbf{r_2})}$ is given by

$$\overline{\delta\rho(\mathbf{r_2})} = \int d\mathbf{r_3} a(|\mathbf{r_2} - \mathbf{r_3}|)[\rho(\mathbf{r_3}) - \rho_0],$$

with the simplest choice of the expression for $a(r)$ given by

$$a(r) = \frac{6}{\pi d^3} \Theta\left(\frac{d}{2} - r\right)$$

where $\Theta(x)$ is the Heaviside step function and is equal to 1 if $r < d/2$ and zero otherwise. The details of this theory are given elsewhere[35]. The above equation is a three dimensional equation and further simplification of the above equation to its one-dimensional form has been done by exploiting the cylindrical symmetry of the problem. For confinement of the colloidal fluid in a cylindrical pore of radius R_0 along the radial direction R for an infinitely long cylinder the same is given by

$$\beta u_{wall}(R) = K_w \frac{I_0(\kappa R)}{I_0(\kappa R_0') - 1}, \qquad \text{for } R < R_0',$$

where R_0 is the distance from the cylinder axis to the point at which a colloidal particle is in contact with the cylinder's inner hard wall such that $R_o' = R_0 - d/2$, I_0 is the modified Bessel function of order zero and K_w is the electrostatic potential energy of a colloidal particle in contact with the cylinder wall with reference to the potential at the center of the cylinder.

Molecular dynamics:

A computer model based on molecular dynamics has been attempted to explain the temporal modulation of local volume fraction vis-à-vis nano-structure assembly during drying of solvent. The computer model primarily focuses on the role of evaporation of two types of water, namely, free water and bound water. In order to resemble the experimentally observed temporal modulation of nano-structure correlation, two phases of solvent evaporation was implemented in the time scale of simulation. The 3D

canonical-NVT (N: Total number of particles, V: Volume, T: Temperature) model consists of an ensemble of monodisperse spherical nanoparticles of definite sizes confined inside a cylindrical channel (radius = 100 nm and length = 1000 nm). The total number of non-overlapping nanoparticles generated inside the cylindrical channel are 18000, 4394 and 820 for S1 (diameter (d) =10 nm), S2 (d =16 nm) and S3 (d = 28 nm) systems, respectively to obtain the volume fraction, φ = 0.3 of the colloidal suspension. The major portion of the solvent present in nano-channel is considered to be free water and the rest portion is the bound water attached to different functional group of silica nanoparticle. In the simulation model, the evaporation of bound water commence only after the entire free water evaporates out. The bound water volume is taken as proportional to total spherical surface area offered by the colloidal particles. The ratio of bound water in S1, S2 and S3 system is calculated as 2.8: 1.8: 1.0, approximately, in accordance with available total nanoparticles surface area of corresponding system. Thus, the free water content of S1 system is least whereas, S3 system has maximum free water content.

In order to incorporate the time co-ordinate (t) in the simulation model, each iteration step is considered to be equivalent to time scale with proper normalization factor. The time co-ordinate is scaled by considering a consistent solvent drying rate (obtained from experimental observation) for each case. The total time ($'\tau'$) of evaporation of free water is estimated for each system. The dynamics of each nanoparticle is monitored by calculating its velocity and acceleration vector by finite difference method by solving Newtonian equation of motion in each iteration step. The inter-particle force is calculated by,

$$\vec{F}_{pair} = -\vec{\nabla} U(r_{ij}), \text{ where } U(r_{ij}) = \left[\mu \frac{e^{-\kappa r_{ij}}}{r_{ij}} - \left(\frac{\sigma}{r_{ij}} \right)^6 \right]$$ is the pair potential as mentioned in the main article.

The local volume fraction has been estimated in respect of updated positional co-ordinates of the colloidal particles. The local volume fraction of the nanoparticles has been calculated using the following formula:

$$\phi = \frac{\sum_i n_i \left(\frac{n_i V_p}{V_i} \right)}{\sum_i n_i}$$

, where 'V_i' being the volume of the ith annular cylinder and 'n' being the number of nanoparticles present in the annular volume V_i. 'V_p' is the volume of a single spherical nanoparticle. The volume of the annular cylindrical region is estimated by the following equation:

$$V_i = \pi(2r_i + dr) \cdot dr \cdot dh$$

, where 'r_i' and 'r_i+dr' being the inner and outer radii of the annular cylindrical region, respectively and 'dh' is the length of each cylinder.

In the first phase of evaporation *i.e.*, during evaporation of free water ($t<\tau$), the total force ($F(r)$) on the particle is $-\vec{\nabla}U(r) - \frac{2\Gamma}{r'}\hat{r}$. The relative strength of capillary pull over inter-particle interaction is considered to be so strong that it perturbs the homogeneous suspension by dragging the colloidal particle radially outward towards the boundary wall of the channel. This results into monotonic rise in local volume fraction of the assembled nano-structure. The maximum value of estimated local volume fraction (~0.6) corresponds to that time co-ordinate ($t = \tau$) when the entire free water dries out and bound water starts to evaporate. At this point of iteration of the simulation model ($t \geq \tau$), the capillary attraction disappears (i.e., $\Gamma\rightarrow0$) and the dormant columbic repulsion becomes active among the nanoparticles. The Coulomb repulsion (assumed to be without screening factor in absence of solvent) tries to loosen up the jamming of the nanoparticles. The nanoparticles undergo re-structuring to balance the inter-particle van der Waal attraction and Coulombic repulsion during evaporation of bound water ($\tau \leq t < \tau'$; τ' being that time co-ordinate when total bound water evaporates out). The nanostructure near the wall boundary becomes more bifurcated due to this relaxation and results in slight reduction of local volume fraction. This continues until the entire bound water dries out and hence, the negative charge of the nanoparticles ceases to exist. At this moment of time ($t \geq \tau'$) vis-à-vis iteration step, the Coulomb force strength is enforced to zero. The neutral nanoparticles then tend to aggregate by van der Waal interaction due to

availability of their large specific surface area and thus, local density of the nanoparticles increases slightly until it saturates.

The force equation, in summary, can be written by splitting all the potential function, contributing in different time domain, as follow:

$$\vec{F}(\vec{r}) = \begin{cases} -\vec{\nabla}u_1 - \vec{\nabla}u_2 - \dfrac{2\Gamma}{r'}\hat{r}, & \forall t < \tau \\ -\vec{\nabla}u_3 - \vec{\nabla}u_2, & \forall \tau \le t < \tau' \\ -\vec{\nabla}u_4 - \vec{\nabla}u_2, & \forall t \ge \tau' \end{cases}$$

, where

$$u_1(r) = \mu \frac{e^{-\kappa r}}{r}$$

$$u_2(r) = -\left(\frac{\sigma}{r_{ij}}\right)^6$$

$$u_3(r) = \frac{\mu}{r}$$

$$u_4(r) = \begin{cases} \infty, & \forall r \le d \\ 0, & \forall r > d \end{cases}, d \ being \ size \ of \ the \ particle$$

It is worthy to note that the maximum value of φ in S1 system reaches earlier to that of S2 and S3. It is due to the fact that S1 system contains least amount of free water volume and hence takes lesser evaporation time to exhaust its free water. The concept of free water corroborates with the experimental result as well, where a linear shift in time corresponding to the peaks of φ is prominent. The modulation of φ can only be explained by proper tuning the relative strength of the capillary attractive force and Coulomb repulsive force in two different phases of evaporation (free water and bound water).