Supplementary Materials:

Probing Evaporation induced Assembly across a Drying Colloidal Droplet using *in situ* Small-Angle X-ray Scattering at Synchrotron Source

D. Sen[1], J. Bahadur[1], S. Mazumder[1], G. Santoro[2], S. Yu[2] and S. V. Roth[2]

[1]*Solid State Physics Division, Bhabha Atomic Research Centre, Mumbai-400085, India*

[2]*Deutsches Elektronen-Synchrotron (DESY), Notkestr. 85, D-22607, Hamburg, Germany*

1. Calculation of Porod invariant using the effective thickness traversed by x-ray beam while passing through a colloidal droplet

i) Spherical droplet with uniform volume fraction ϕ of colloids:

$(AB)^2=R^2-x^2$

Effective thickness=2AB So, Porod invariant(Q) $\propto \phi.(1-\phi)2AB= \phi.(1-\phi)\,(R^2-x^2)^{0.5}$

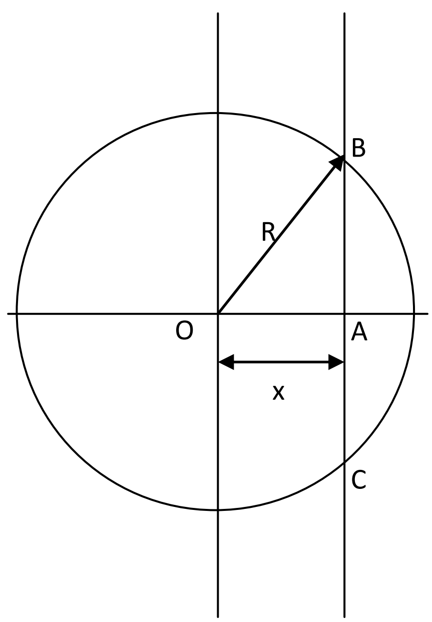

Fig. Supp. 1. Calculation of Porod invariant across a droplet with uniform volume fraction of colloids.

Electronic Supplementary Material (ESI) for Soft Matter

ii) Hollow Spherical grain:

$(AB)^2=R_o^2- R_i^2$

For $x<R_i$, $(MP)^2=R_o^2-x^2$

MP=MN+NP and $(MN)^2=R_i^2-x^2$ and $(MP)^2-(MN)^2=R_o^2-R_i^2$

So, Porod invariant $\propto 2\ \phi_2(1- \phi_2)\ (MP-MN)=2\ \phi_2(1- \phi_2)\ (R_o^2-R_i^2)/(MP+MN)$

$= 2\phi_2(1- \phi_2)\ (R_o^2-R_i^2)/\ [(R_o^2-x^2)^{0.5}+(R_i^2-x^2)^{0.5}]$

For $R_i <x < R_o$, then

Porod invariant $\propto 2\phi_2(1- \phi_2)\ (R_o^2-x_i^2)^{0.5}$

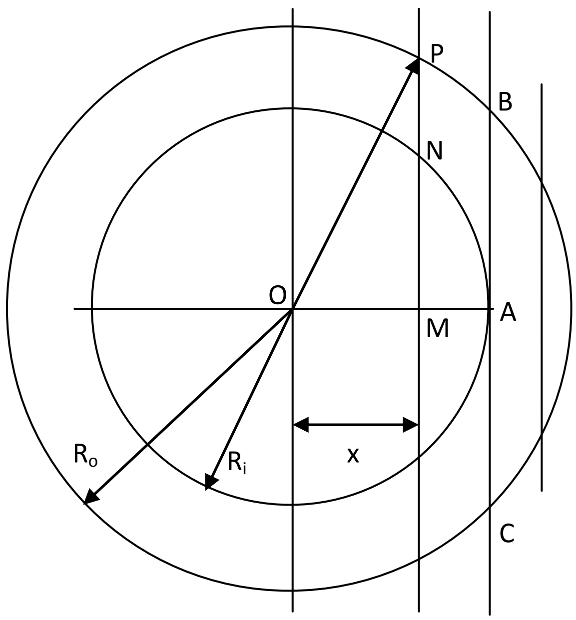

Fig. Supp. 2. Porod invariant in case of hollow spherical grain.

iii) Core and shell at different volume fraction (ϕ_1 and ϕ_2 , respectively) :

Porod invariant $\propto$ [2(MP-MN) $\phi_2(1-\phi_2)$+(2MN) $\phi_1(1-\phi_1)$]

For **$x<R_i$**,

Porod invariant $\propto 2\phi_1(1-\phi_1)(R_i^2-x^2)^{0.5}+2\phi_2(1-\phi_2)(R_o^2-R_i^2)/[(R_o^2-x^2)^{0.5}+(R_i^2-x^2)^{0.5}]$

For $R_i<x<R_o$,

Porod invariant $\propto 2\phi_2(1-\phi_2)(R_o^2-x^2)^{0.5}$

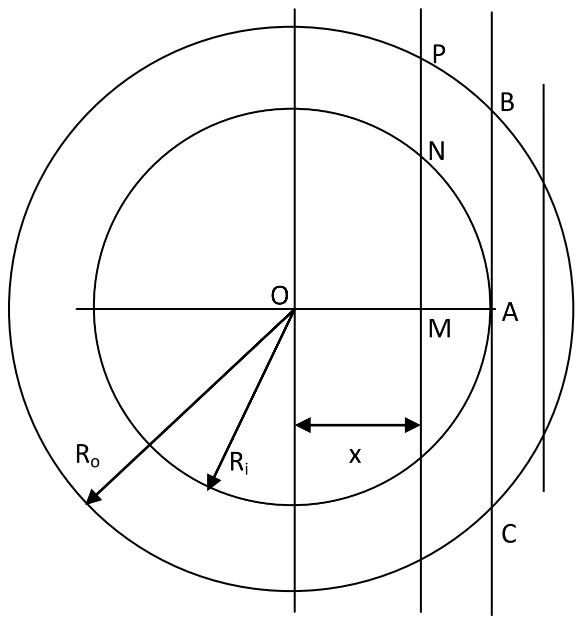

Fig. Supp. 3. Calculation of Porod invariant for the situation where core and shell are at different volume fractions of colloids.

Electronic Supplementary Material (ESI) for Soft Matter

Form factor and structure factor of colloids for standard experiments performed using colloids in capillary tube:

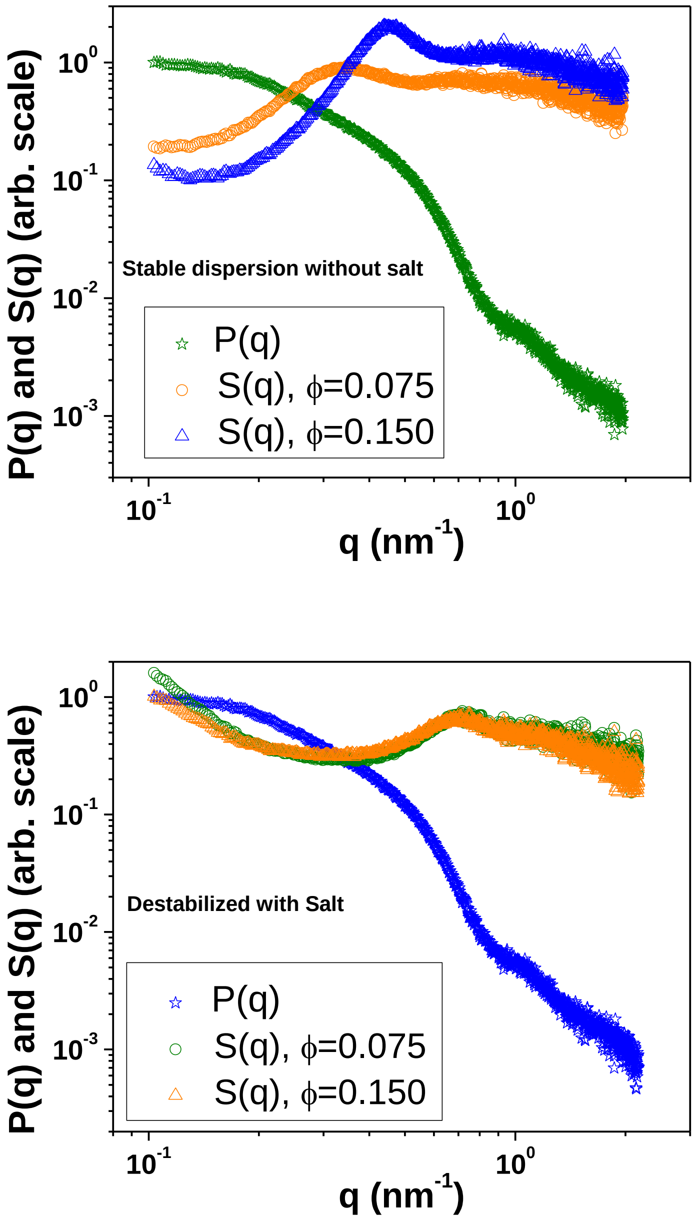

Fig. supp. 4. (Top)*Form factor and structure factor of the stable dispersion.* (Bottom) *Form factor and structure factor of the NaCl destabilized LUDOX dispersion.*

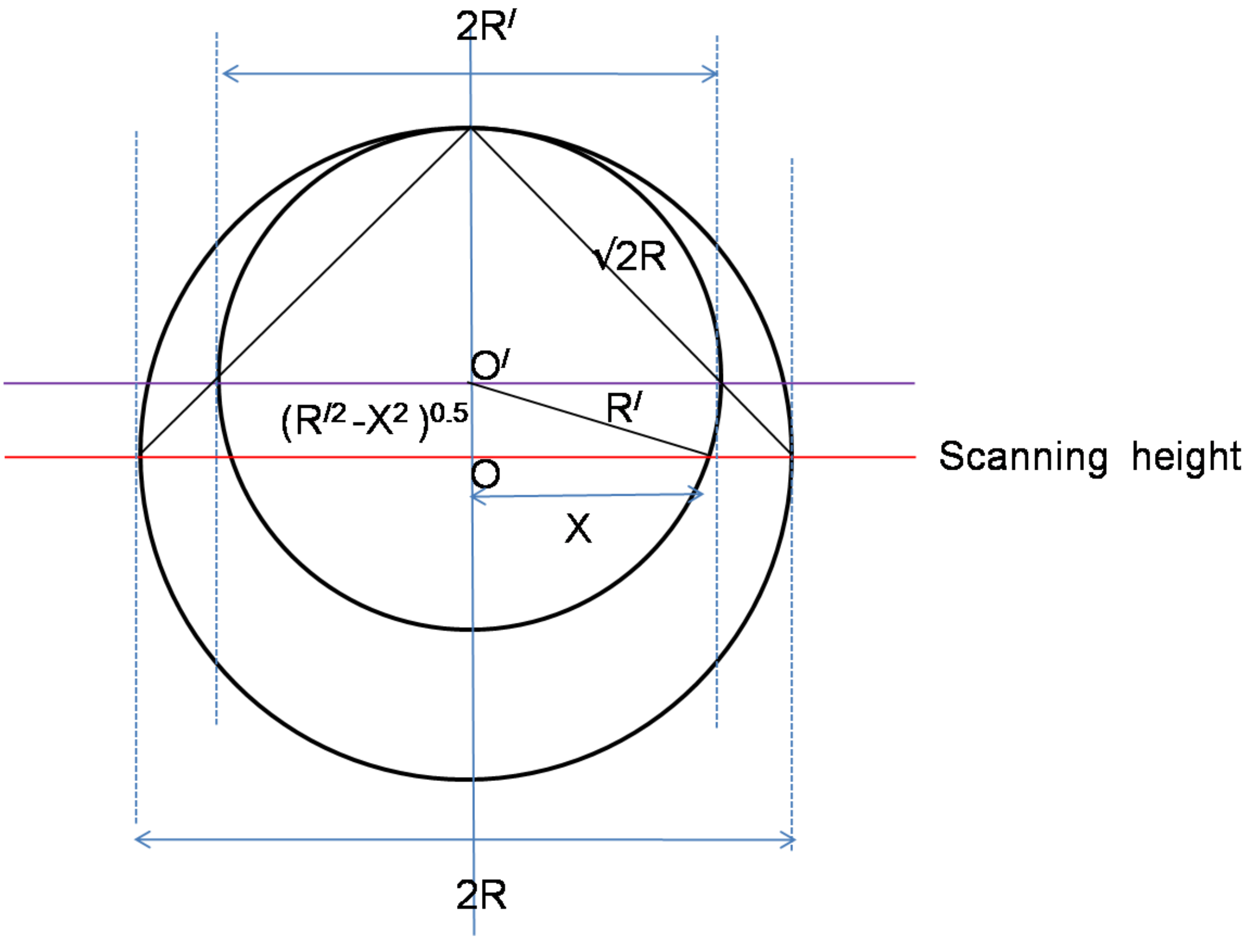

Fig. supp. 5. *Schematic diagram illustrating r elation between the droplet thickness measured at any time and its actual radius at that time.*

At time t=0, the horizontal scanning measures the diameter (2R) of the droplet. At other time a chord (2X) other than the diameter (2R$^{/}$) is measured. To correlate the measured length 2X with diameter at that time one can use the following formula. From the above figure, $R - R^{/} = \sqrt{R^{/2} - X^{2}}$

and thus

$R^{/} = \dfrac{R^{2} + X^{2}}{2R}$. So, one can estimate the diameter at later time from the measure value of X.

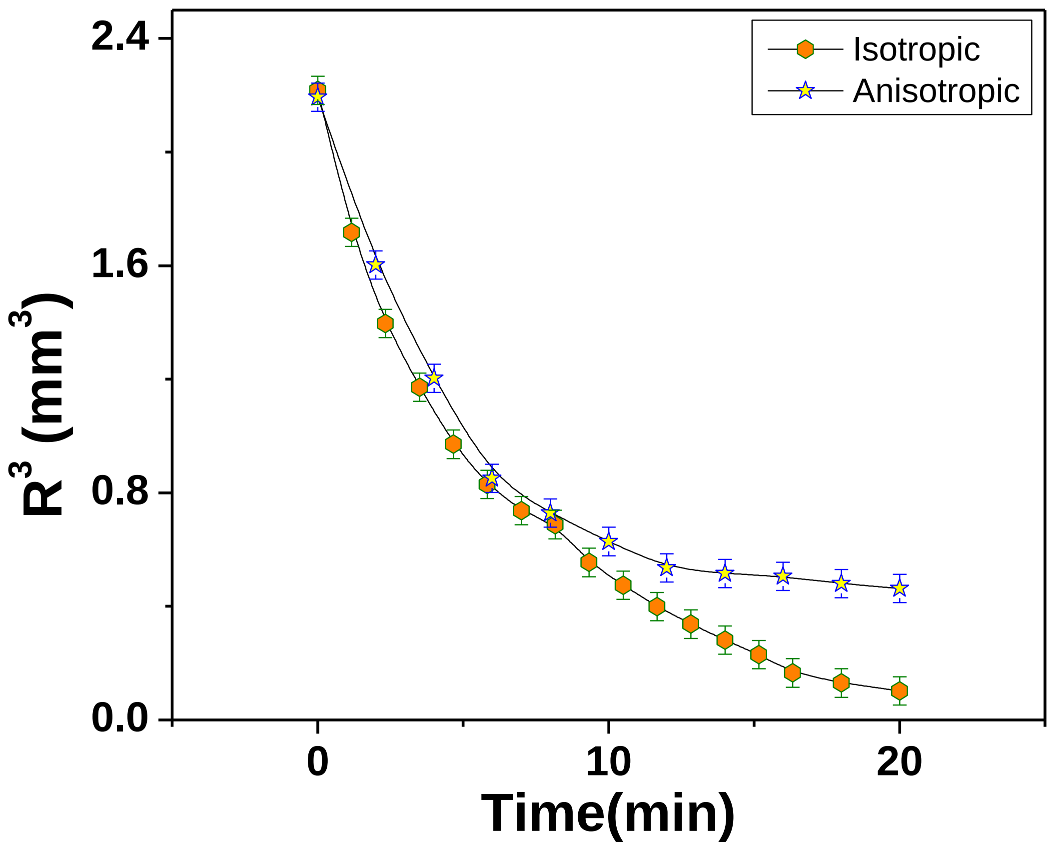

Fig. supp. 6. *Variation of external droplet volume with time in isotropic and anisotropic cases.*

Calculation of initial colloidal concentration required to completely coat the surface of a droplet

From the conservation of particle number in the droplet, one gets

$$\phi_{shell}(t) = \frac{\phi_0 R_0^3 - \phi_{core}(t) R_{in}^3(t)}{[R_{out}^3(t) - R_{in}^3(t)]}$$

To estimate the lowest concentration required for the shell formation at t=0, it is assumed that all the nanoparticles take part in shell formation to completely coat the droplet surface by forming monolayer leaving no particle in the core. , In this case, $R_{in}=R_o-2r_p$. $\phi_{shell}=\phi_c$ (critical concentration) and $\phi_{core}=0$. The expression for f_0 can be as estimated from the above equation as follows

$$\phi_0 = \frac{\phi_c \left(R_0^3 - (R_0 - 2r_p)^3 \right)}{R_0^3}$$

If R_0=1.5 mm, r_p=5 nm, ϕ_c is taken to be 0.74, then the value of ϕ_0 in this case becomes 1.5x 10^{-5}. We would like to point out that such a case can happen only with extremely fast drying without shrinkage of droplet, where all particles immediately can form a shell leaving no particle at core.