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Supporting information for article:

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Debasis Sen, Ashwani Kumar, Avik Das and Jitendra Bahadur

Supplementary document

Estimation and Fingerprinting of Size-distribution of Non-Interacting Spherical Particles from Small-Angle Scattering Data

Debasis Sen[1,2], Ashwani Kumar[1], Avik Das[1,2], Jitendra Bahadur[1,2]

[1]Solid State Physics Division, Bhabha Atomic Research Centre

[2]Homi Bhabha National Institute, Anushaktinagar, Mumbai-400094, India

**Corresponding author: Tel: +91-22-25594608; Fax:+91-22-25505151*

Email: *debasis@barc.gov.in*; *debasis.sen@gmail.com*

Derivation considering Lognormal distribution:

Let the scattering intensity be I(q). In fact, from the standard definition of the intensity,

$$I(q) = (\Delta\rho)^2 \frac{\int_0^\infty P(q) D(r) V^2(r) dr}{\int_0^\infty D(r) V(r) dr} = (\Delta\rho)^2 \frac{\int_0^\infty \frac{9(\sin(qr) - qr\cos(qr))^2}{(qr)^6} D(r) V^2(r) dr}{\int_0^\infty D(r) V(r) dr}$$

Thus, $I(q) = (\Delta\rho)^2 \left(12\pi\right) \frac{\int \frac{(\sin(qr) - qr\cos(qr))^2}{(q^6 r^6)} D(r) r^6 dr}{\int D(r) r^3 dr}$

The denominator of the above equation is a q independent term.

Thus, I(q) is proportional to $\int \frac{(\sin(qr) - qr\cos(qr))^2}{(q^6)} D(r) dr$

So, $I(q) \propto \int \frac{(\sin(qr) - qr\cos(qr))^2}{(q^6)} D(r) dr$

The integration in the above equation is on r and hence by rearranging q^4 term,

$$I(q) q^4 \propto \int \frac{(\sin(qr) - qr\cos(qr))^2}{(q^2)} D(r) dr \qquad \text{.......... (1)}$$

At the peak ($q=q_{peak}$) in the Porod plot

$$\frac{\partial}{\partial q}\left(I(q) q^4\right) \sim \frac{\partial}{\partial q}\left(\int \frac{(\sin(qr) - qr\cos(qr))^2}{(q^2)} D(r) dr\right) = 0 \qquad \text{....................(2)}$$

$$\left(\int_0^\infty \frac{q^2\left(2(\sin(qr)-qr\cos(qr))(r\cos(qr)+qr^2\sin(qr)-r\cos(qr))\right)-2q(\sin(qr)-qr\cos(qr))^2}{q^4}D(r)dr\right)=0$$

$$\left(\int_0^\infty\left(\frac{q^3r^2\sin(qr)(\sin(qr)-qr\cos(qr))-q(\sin(qr)-qr\cos(qr))^2}{q^4}\right)D(r)dr\right)=0$$

$$\left(\int_0^\infty q^2r^2\sin(qr)(\sin(qr)-qr\cos(qr))-(\sin(qr)-qr\cos(qr))^2 D(r)dr\right)=0$$

for $q=q_{peak}$

For a lognormal distribution

$$D(r)=\left(\frac{1}{\sqrt{2\pi}\sigma r}\right)\exp\left(-\frac{(\ln(r/R_m))^2}{2\sigma^2}\right)dr$$

Let us consider $r/R_m=x$

$$\left(\int_0^\infty (q_pR_mx)^2\sin(q_pR_mx)(\sin(q_pR_mx)-q_pR_mx\cos(q_pR_mx))-(\sin(q_pR_mx)-q_pR_mx\cos(q_pR_mx))^2R_mD(x)dx\right)=0$$

Let us put $q_{peak}*R_m=K$

$$\left(\int_0^\infty K^2x^2\sin(Kx)(\sin(Kx)-Kx\cos(Kx))-(\sin(Kx)-Kx\cos(Kx))^2R_m\left(\frac{1}{\sqrt{2\pi}xR_m}\right)\exp\left(-\frac{(\ln(x))^2}{2\sigma^2}\right)dx\right)=0$$

The integration is over x as dummy variable, so the resulting integral will depend on *K* and σ only.

Thus, the above Function(K,σ)=0, so *K* is a function of σ only and does not depend on R_m. So, *K=K(σ)*

(This is also verified from the simulation that the quantity $q_p^2R_m^2$ depends only on σ and is independent of R_m)

Thus, $q_{peak}*R_m=K(\sigma)$, i.e., $q_{peak}*R_m$ and depends on σ only,

Now,

$$\int_0^\infty D(r)r^3dr\times\left(I(q)q^4\right)=(12\pi)(\Delta\rho)^2q^4\int_0^\infty\frac{(\sin(qr)-qr\cos(qr))^2}{(qr)^6}D(r)r^6dr$$

$$\int_0^\infty D(r)r^3dr \times \left(I(q)q^4\right) = (12\pi)(\Delta\rho)^2 q^4 \int_0^\infty \frac{(\sin(qr) - qr\cos(qr))^2}{(q)^6} D(r)dr$$

$$\int_0^\infty D(r)r^3dr \times \left(I(q)q^4\right) = (12\pi)(\Delta\rho)^2 (K/R_m)^4 \int_0^\infty \frac{(\sin(xK) - x\cos(xK))^2}{(K/R_m)^6} D(xR_m)R_m dx$$

$$\int_0^\infty D(r)r^3dr \times \left(I(q)q^4\right) = (12\pi)(\Delta\rho)^2 \int_0^\infty \frac{(\sin(xK) - x\cos(xK))^2}{(K/R_m)^2} \left(\frac{1}{\sqrt{2\pi}xR_m}\right) \exp\left(-\frac{(\ln(x))^2}{2\sigma^2}\right) R_m dx$$

$$\int_0^\infty D(r)r^3dr \times \left(I(q)q^4\right) = (12\pi)(\Delta\rho)^2 (R_m)^2 \int_0^\infty \frac{(\sin(xK) - x\cos(xK))^2}{K^2} \left(\frac{1}{\sqrt{2\pi}x}\right) \exp\left(-\frac{(\ln(x))^2}{2\sigma^2}\right) dx$$

Let us assume $\boxed{f(\sigma) = (12\pi) \int_0^\infty \frac{(\sin(xK) - x\cos(xK))^2}{K^2} \left(\frac{1}{\sqrt{2\pi}x}\right) \exp\left(-\frac{(\ln(x))^2}{2\sigma^2}\right) dx}$ ....(3)

So $\int_0^\infty D(r)r^3dr \times \left(I(q)q^4\right) = (\Delta\rho)^2 (R_m)^2 f(\sigma)$ Thus, $\left(I(q)q^4\right) = (\Delta\rho)^2 (R_m)^2 f(\sigma) / (\int_0^\infty D(r)r^3dr)$

Now $\int_0^\infty D(r)r^3dr = R_m^{\;3} \exp(9\sigma^2/2)$ So, $\left(I(q_{peak})q_{peak}^{\;4}\right) = (1/R_m) f(\sigma) / (\exp(9\sigma^2/2))$

Now $\Sigma_P = I(q_{Porod})q_{Porod}^{\;4} = (2\pi)(\Delta\rho)^2 \frac{S}{V} = (2\pi)(\Delta\rho)^2 c \frac{<r^2>}{<r^3>} = (2\pi)(\Delta\rho)^2 c \frac{R_m^{\;2} \exp(4\sigma^2/2)}{R_m^{\;3} \exp(9\sigma^2/2)}$

$$I(q_{Porod})q_{Porod}^{\;4} = (2\pi)(\Delta\rho)^2 c \frac{R_m^{\;2} \exp(4\sigma^2/2)}{R_m^{\;3} \exp(9\sigma^2/2)} = (2\pi)(\Delta\rho)^2 c \frac{\exp(-2.5\sigma^2)}{R_m}$$

So, $\frac{I(q_{Peak})q_{Peak}^{\;4}}{I(q_{Porod})q_{Porod}^{\;4}} = \left((R_m^{\;-1}) f(\sigma) / (\exp(9\sigma^2/2))\right) \left((2\pi)c \frac{\exp(-2.5\sigma^2)}{R_m}\right)^{-1}$

$$\frac{I(q_{Peak})q_{Peak}^{\;4}}{I(q_{Porod})q_{Porod}^{\;4}} = \left(f(\sigma) \times (\exp(9\sigma^2/2))^{-1}\right) \left((2\pi)c\exp(-2.5\sigma^2)\right)^{-1}$$

$$\boxed{\frac{I(q_{Peak})q_{Peak}^{\;4}}{I(q_{Porod})q_{Porod}^{\;4}} = \frac{I(q_{Peak})q_{Peak}^{\;4}}{\Sigma_P} = (c2\pi)^{-1} f(\sigma)\left(\exp(-2\sigma^2)\right)}$$ ....(4)

This shows that the ratio is independent of R_m and depends on σ only.

Let us try to approximate how the quantity q_{peak}*R_m behaves:

$$I(q)q^4 \propto (12\pi) \int (\Delta\rho)^2 \frac{(\sin(qr) - qr\cos(qr))^2}{(q^2)} D(r)dr$$

First we will see the behavior with a Guinier approximation,

$$I(q)q^4 \propto q^4 \exp(-q^2 \frac{1}{3} rg^2)$$

$$\frac{\partial}{\partial q}\left(I(q)q^4\right) \propto 4q^3 \exp(-q^2 \frac{1}{3} rg^2) - 2q^5 \frac{1}{3} rg^2 \exp(-q^2 \frac{1}{3} rg^2)$$

At the maximum

$2q^3 - q^5 \frac{1}{3} rg^2 = 0$, i.e $q^2 rg^2 = 6$ Now $rg^2 = \frac{3}{5}\frac{\langle r^8 \rangle}{\langle r^6 \rangle}$

Now for Lognormal distribution, n^{th} moment is given by

$$\langle r^n \rangle = R_m{}^n \exp(n^2\sigma^2 / 2)$$

$$\boxed{q_{peak}^2 R_m^2 \propto C \exp(-D\sigma^2)} \quad ....(5)$$

However, this is based on the approximation that the maximum occur at small enough q value, which is not exactly true.

Thus, we assume a more general form that fits the variation of $q_{peak}{}^2 R_m{}^2$ and we try to estimate these unknown coefficients from the fit of the variation of this quantity with σ.

$$\boxed{K(\sigma)^2 = q_{Peak}^2 R_m^2 = C_1 + C_2 \exp(-D_2\sigma^2) + C_3 \exp(-D_3\sigma^2) + ...} \quad ... (6)$$

where C_1, C_2, ...D_2,.... are some constants that needs to be determined.

It is already shown that

$$\boxed{\frac{I(q_{Peak})q_{Peak}{}^4}{I(q_{Porod})q_{Porod}{}^4} = (c2\pi)^{-1} f(\sigma)\left(\exp(-2\sigma^2)\right)}$$

where

$$\boxed{f(\sigma) = (4\pi/3)^3 \int_0^\infty \frac{(\sin(xK) - x\cos(xK))^2}{K^2}\left(\frac{1}{\sqrt{2\pi x}}\right)\exp(-\frac{(\ln(x))^2}{2\sigma^2})dx} \quad ....(7)$$

Please note that equation 7 is also similar to equation 2 but here *q* gets replaced by *K*. It should be also noted that $q_{peak}R_m = K(\sigma)$. This means that with R_m=1, one can approximate the functional form of f(σ) as of K.

Thus, the ratio T can also be represented in the similar form .

Thus, in summary,

$$T = \frac{I(q_{Peak})q_{Peak}{}^{4}}{\Sigma_P} \approx F_1 + F_2\exp(-G_2\sigma^2) + F_3\exp(-G_3\sigma^2) + \ldots\ldots$$ ....(8)

$$q_{Peak}^2 R_m^2 = K(\sigma)^2 = C_1 + C_2\exp(-D_2\sigma^2) + C_3\exp(-D_3\sigma^2) + \ldots\ldots$$ ...... (9)

The values of the quantities F_1,F_2,F_3, G_2,G_3 and C_1,C_2,C_3,D_2 and D_3 have been determined from the fitting from the fitting of the variation of *T* and $q_{peak}{}^2R_m{}^2$ with σ, as obtained from the simulation.

Derivation considering Weibull distribution:

For a Weibull distribution

$$D_{WB}(r) = \left(\frac{\kappa}{\lambda}\right)\left(\frac{r}{\lambda}\right)^{(k-1)} \exp\left[-\left(\frac{r}{\lambda}\right)^{k}\right]$$ ....(10)

Let us consider $r/R_m=x$ and let $\lambda=R_m$

$$\left(\int_0^\infty (q_pR_mx)^2\sin(q_pR_mx)(\sin(q_pR_mx) - q_pR_mx\cos(q_pR_mx)) - (\sin(q_pR_mx) - q_pR_mx\cos(q_pR_mx))^2 R_m D(x)dx\right) = 0$$

Let us put $q_p*R_m=K$

$$\left(\int_0^\infty K^2x^2\sin(Kx)(\sin(Kx) - Kx\cos(Kx)) - (\sin(Kx) - Kx\cos(Kx))^2 R_m\left(\frac{\kappa}{R_m}\right)(x)^{(k-1)}\exp\left[-(x)^k\right]dx\right) = 0$$

The integration is over x, so the resulting integral will depend on K and σ only.

Thus, the above Function(K,σ)=0, so K is a function of σ only and does not depend on Rm.

So, K=K(σ) (This should also be verified from simulation that the product q_pR_m depends only on σ and is independent of R_m)

Thus, $q_{peak}*R_m$=K(σ), i.e., $q_{peak}*R_m$ and depends on σ only,

$$\int_0^\infty D(r)r^3dr \times \left(I(q)q^4\right) = (12\pi)(\Delta\rho)^2 q^4 \int_0^\infty \frac{(\sin(qr) - qr\cos(qr))^2}{(qr)^6} D(r)r^6 dr$$

$$\int_0^\infty D(r)r^3dr \times \left(I(q)q^4\right) = (12\pi)(\Delta\rho)^2 q^4 \int_0^\infty \frac{(\sin(qr)-qr\cos(qr))^2}{(q)^6} D(r)dr$$

$$\int_0^\infty D(r)r^3dr \times \left(I(q)q^4\right) = (12\pi)(\Delta\rho)^2 (K/R_m)^4 \int_0^\infty \frac{(\sin(xK)-x\cos(xK))^2}{(K/R_m)^6} D(xR_m)R_m dx$$

$$\int_0^\infty D(r)r^3dr \times \left(I(q)q^4\right) = (12\pi)(\Delta\rho)^2 \int_0^\infty \frac{(\sin(xK)-x\cos(xK))^2}{(K/R_m)^2} \left(\frac{\kappa}{R_m}\right)(x)^{(k-1)} \exp\left[-(x)^k\right] R_m dx$$

$$\int_0^\infty D(r)r^3dr \times \left(I(q)q^4\right) = (12\pi)(\Delta\rho)^2 (R_m)^2 \int_0^\infty \frac{(\sin(xK)-x\cos(xK))^2}{K^2} (\kappa)(x)^{(k-1)} \exp\left[-(x)^k\right] dx$$

Let us assume $\boxed{f(\kappa) = (12\pi)\int_0^\infty \frac{(\sin(xK)-x\cos(xK))^2}{K^2} (\kappa)(x)^{(k-1)} \exp\left[-(x)^k\right] dx}$

So $\int_0^\infty D(r)r^3dr \times \left(I(q)q^4\right) = (\Delta\rho)^2 (R_m)^2 f(\kappa)$ Thus, $\left(I(q)q^4\right) = (\Delta\rho)^2 (R_m)^2 f(\kappa) / (\int_0^\infty D(r)r^3dr)$

Now $\int_0^\infty D(r)r^3dr = R_m^{\ 3}\Gamma\left(1+\frac{3}{\kappa}\right)$ So, $\boxed{\left(I(q_{peak})q_{peak}^{\ 4}\right) = (1/R_m) f(\kappa) / \Gamma\left(1+\frac{3}{\kappa}\right)}$

Now $I(q_{Porod})q_{Porod}^{\ 4} = (2\pi)(\Delta\rho)^2 \frac{S}{V} = (2\pi)(\Delta\rho)^2 c \frac{<r^2>}{<r^3>} = (2\pi)(\Delta\rho)^2 c \frac{R_m^{\ 2}\Gamma\left(1+\frac{2}{\kappa}\right)}{R_m^{\ 3}\Gamma\left(1+\frac{3}{\kappa}\right)}$

$$\boxed{I(q_{Porod})q_{Porod}^{\ 4} = (2\pi)(\Delta\rho)^2 c \frac{R_m^{\ 2}\Gamma\left(1+\frac{2}{\kappa}\right)}{R_m^{\ 3}\Gamma\left(1+\frac{3}{\kappa}\right)} = (2\pi)(\Delta\rho)^2 c \frac{\Gamma\left(1+\frac{2}{\kappa}\right)}{\Gamma\left(1+\frac{3}{\kappa}\right)R_m}} \quad \text{............................(11)}$$

So, $\frac{I(q_{Peak})q_{Peak}^{\ 4}}{I(q_{Porod})q_{Porod}^{\ 4}} = (2\pi c)^{-1} \left(\frac{f(\kappa)}{\Gamma\left(1+\frac{2}{\kappa}\right)}\right)$

$$\boxed{\frac{I(q_{Peak})q_{Peak}^{\ 4}}{I(q_{Porod})q_{Porod}^{\ 4}} = (c2\pi)^{-1} f(\kappa)\left(\Gamma\left(1+\frac{2}{\kappa}\right)\right)^{-1}} \quad \text{............................(12)}$$

This shows that the ratio is independent of λ and depends on κ only.

Similar to the Lognormal case, here the two quantities can be represented in the form

$$T = \alpha_0 - (\alpha_0 - \alpha_1)\exp(-(\alpha_2 \kappa)^{\alpha_3}) \qquad \text{........................(13)}$$

$$q_{peak}\lambda^2 = \beta_0 - (\beta_0 - \beta_1)\exp(-(\beta_2 \kappa)^{\beta_3}) \qquad \text{.....................(14)}$$

The values of the quantities α_0, α_0, α_1, α_2, α_3, and β_0, β_1, β_2, β_3, have been determined from the fitting of the variation of *T* and $q_{peak}\lambda^2$ with κ, as obtained from the simulation.

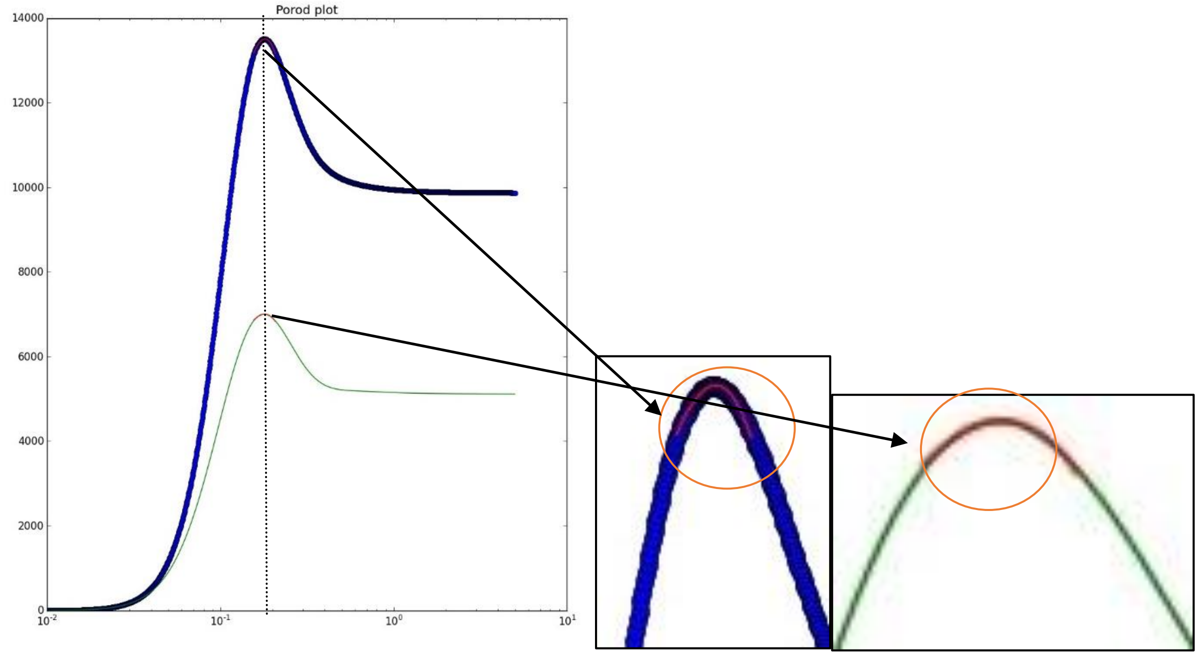

Fig. S1. Correction factor is estimated from the ratio of the width of the peak. The peak zone was fitted with Gaussian function (Zoomed right panels).

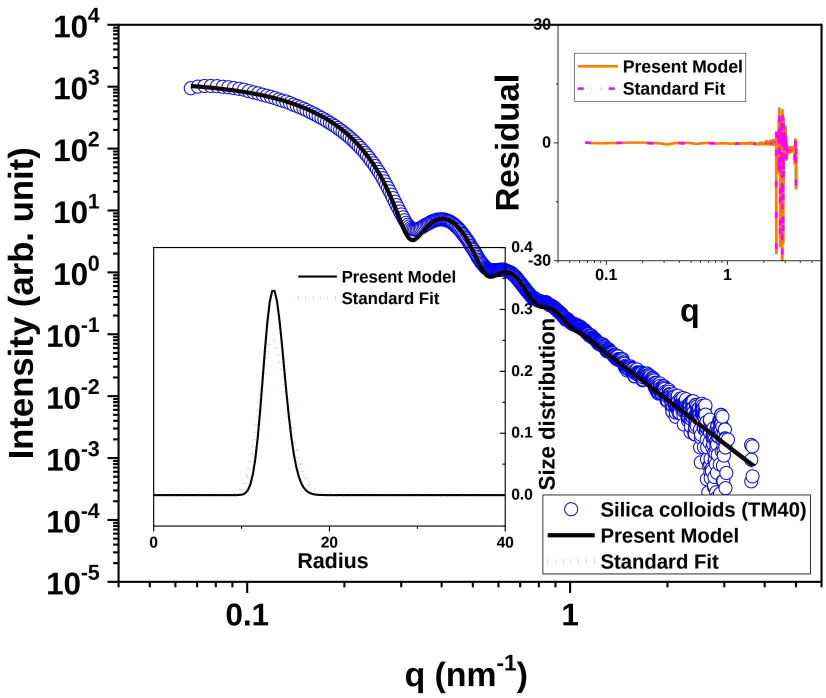

Fig. S2. Comparison of fit with standard non-linear least square model and the present model for TM 40 colloids. The goodness of fit for present model was ~0.99 while that for the standard fit was ~0.98. the standard χ^2 value for present model was 3.4 while that for the standard fit was 3.1.

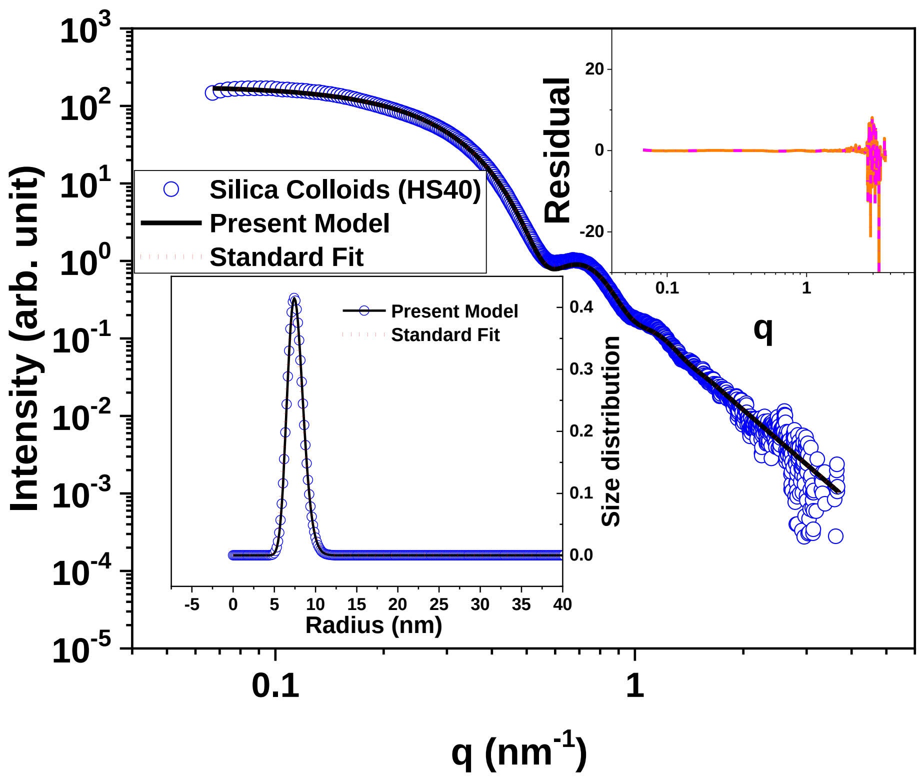

Fig. S2a. Comparison of fit with standard non-linear least square model and the present model for SM 40 colloids. The goodness of fit for present model was ~0.98 while that for the standard fit was 0.97. the standard χ^2 value for present model was 0.7 while that for the standard fit was 0.6.

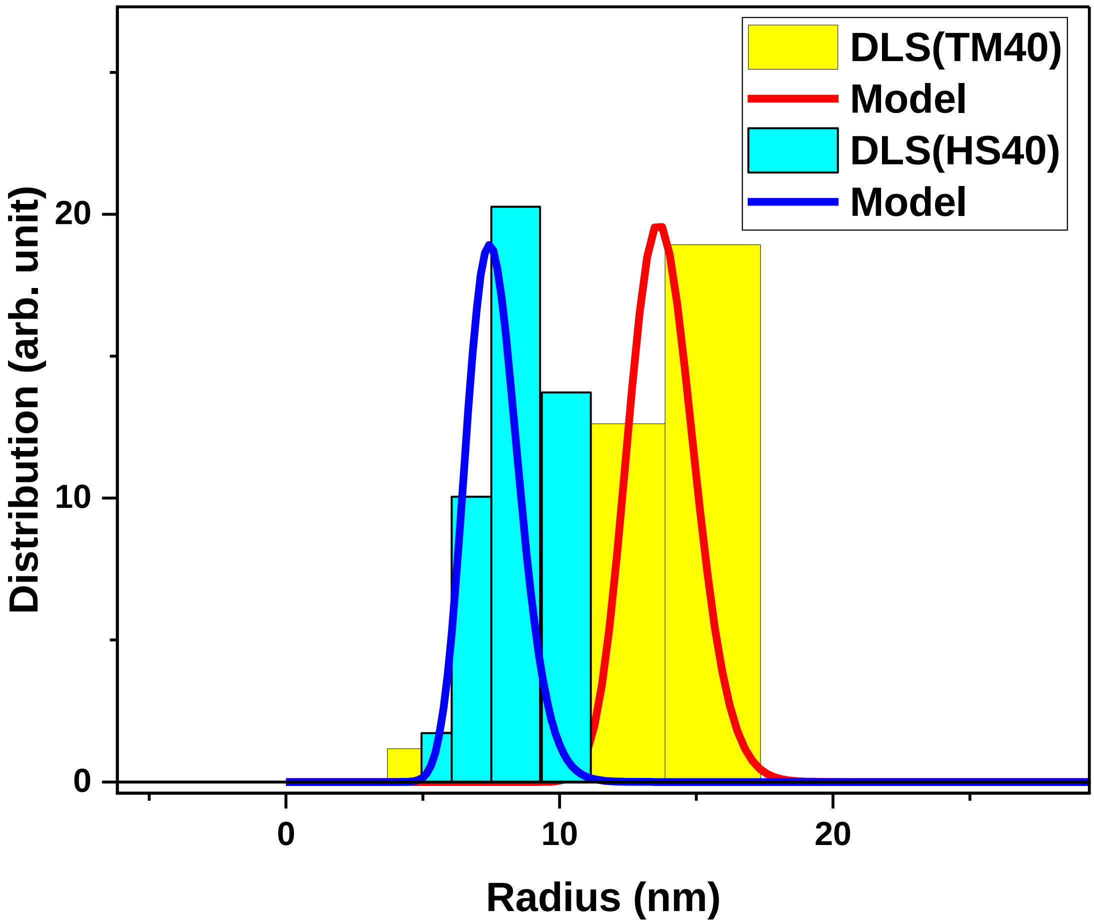

Fig. S3. Comparison of the distributions obtained from the present method and the dynamic light scattering (DLS) method.

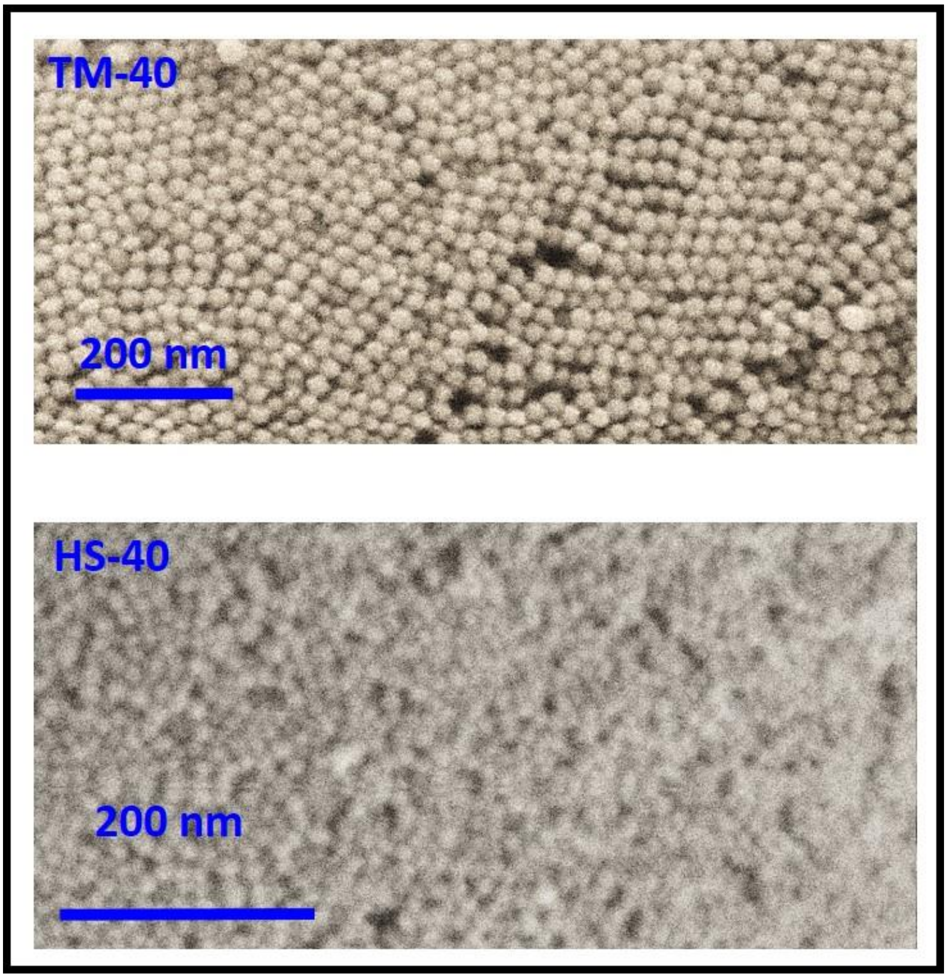

Fig. S4. Field-Emission Scanning Electron Micrograph of the dried silica colloids. FESEM measurements have been performed using Carl Zeiss FESEM.