# The Phase Diagram of Colloidal Silica-PNIPAm core-shell Nanogels - Supplementary Information

Lara Frenzel,*[a,b] Felix Lehmkühler,[a,b] Michael Koof,[a,b], Irina Lokteva,[a,b] and Gerhard Grübel,[a,b]

This supplementary material provides details on the $q$ dependency of the $g_2$ functions of sample $SP_1$ with $\Phi_{eff,20} = 0.15$ at $T = 36°C$, 38°C and 40°C (Fig. 1), the temperature dependency of the Kohlrausch-Williams-Watts (KWW) exponent $\gamma$ (see Eq. 2) of sample $SP_1$ at $\Phi_{eff,20} = 0.12, 0.15, 0.18$ (Fig. 2), the change of the calculated effective volume fraction with increasing temperature (Fig. 3) and the temperature-dependency of the exponents $p$ and $\gamma$ of $SP_1$, $SP_{2B}$ and $SP_{2C}$ (Fig. 4). The KWW exponent has been obtained by averaging over $q$ between $0.006\,nm^{-1} < q < 0.037\,nm^{-1}$ where it shows a slight $q$ dependency as described elsewhere[1]. The errorbars represent the standard deviation of $\gamma$ in this $q$ range. In Fig. 2 $\gamma$ of $SP_1$ at $\Phi_{eff,20} = 0.18$ is plotted for $T < 38°C$ only, since the $g_2$ functions at $T \geq 38°C$ decorrelate only by 1% within the total exposure time of 1.5s. For $SP_1$ with $\Phi_{eff,20} = 0.15$ $\gamma_1$ is shown for $T \geq 38°C$, relating to the faster relaxation process in the system.

Note that in Fig. 3 the values of $\Phi_{eff}$ have been extrapolated from single-particle measurements via dynamic light scattering. Fig. 3b shows the radius and $\Phi_{eff}$ of sample $SP_{2C}$. Here, the calculated volume fraction at 20°C is above 1 whereas it is about 0.1 at 42°C. The real volume fractions of the systems are unknown due to potentially deformed or compressed particle shells at high concentrations[2–4]. For that reason we decided to classify the systems via the value of $\Phi_{eff,20}$ for swollen single particles at 20°C. The temperature dependence of the exponents $p$ and $\gamma$ is shown in Fig. 4 for three sample ($SP_1$ with $\Phi_{eff,20} = 0.14$, $SP_{2B}$ with $\Phi_{eff,20} = 0.55$ and $SP_{2C}$ with $\Phi_{eff,20} = 0.73$). For instance for $SP_1$, the results at 42°C correspond to the rearrangement phase, where the low $\gamma$ value corresponds to the faster decay. At 45°C, no $p$ and $\gamma$ could be reported because the sample was static on the time scale studied (i.e. in the gel phase).

## Supplementary Figures

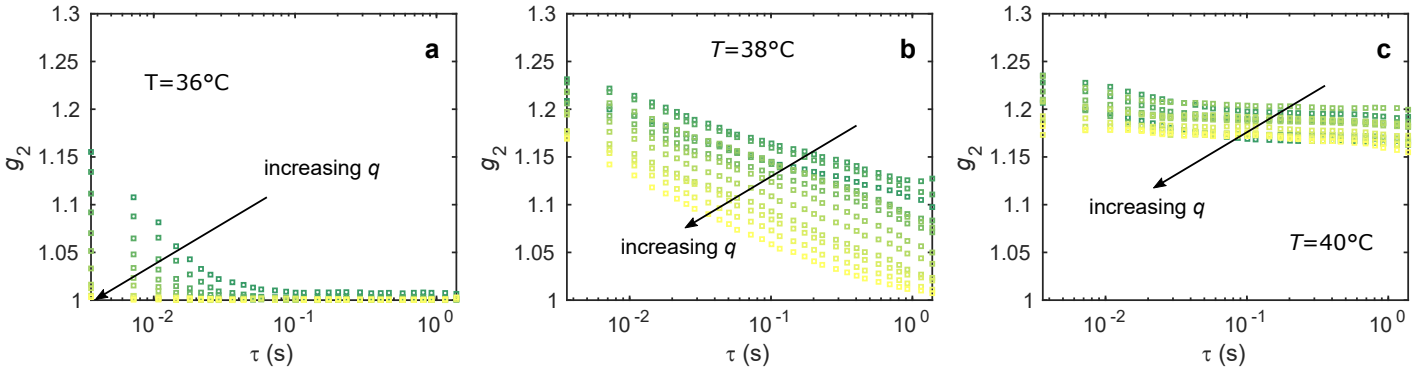


**Fig. 1** $g_2$ functions of $SP_1$ with $\Phi_{eff,20} = 0.15$ at $T = 36°C$, 38°C and 40°C for $0.006\,nm^{-1} < q < 0.037\,nm^{-1}$.

[a] Deutsches Elektronen-Synchrotron DESY, Notkestraße 85, 22607 Hamburg, Germany. E-mail: lara.frenzel@desy.de
[b] The Hamburg Centre for Ultrafast Imaging CUI, Luruper Chaussee 149, 22761 Hamburg, Germany.

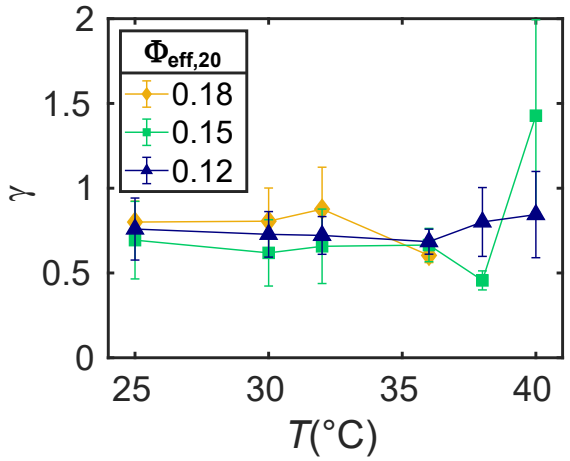


**Fig. 2** Temperature-dependent KWW exponents $\gamma$ of sample $SP_1$ at $\Phi_{eff,20} = 0.12, 0.15, 0.18$.

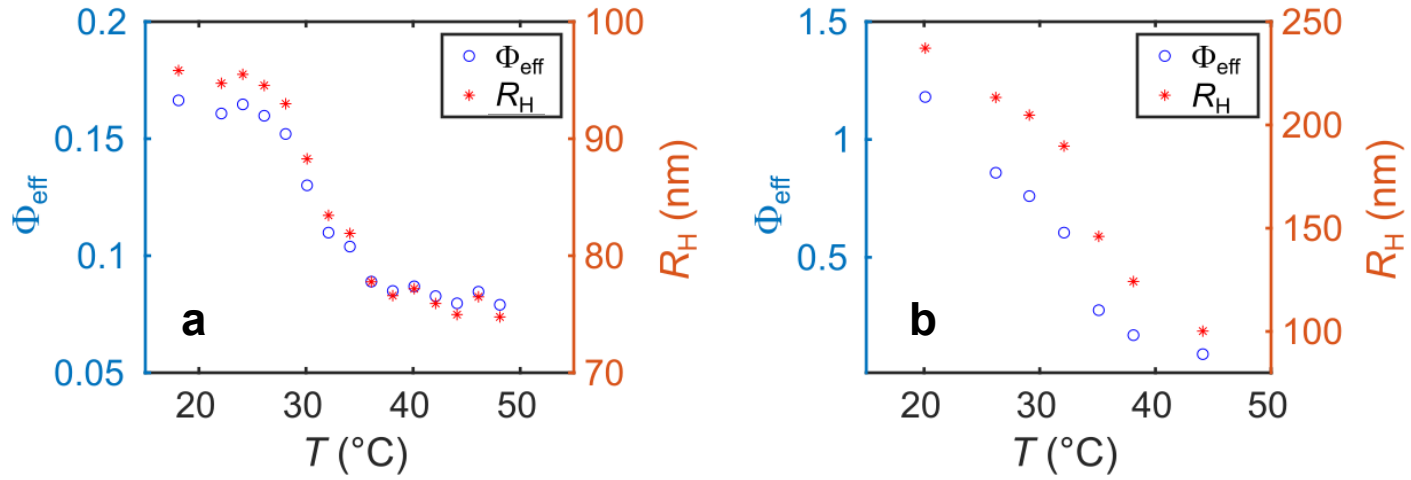


**Fig. 3** Hydrodynamic radius $R_H$ (left axis) of the single particle and the calculated $\Phi_{eff}$ of a concentrated system (right axis) as a function of temperature for a) $SP_1$ and b) $SP_{2C}$.

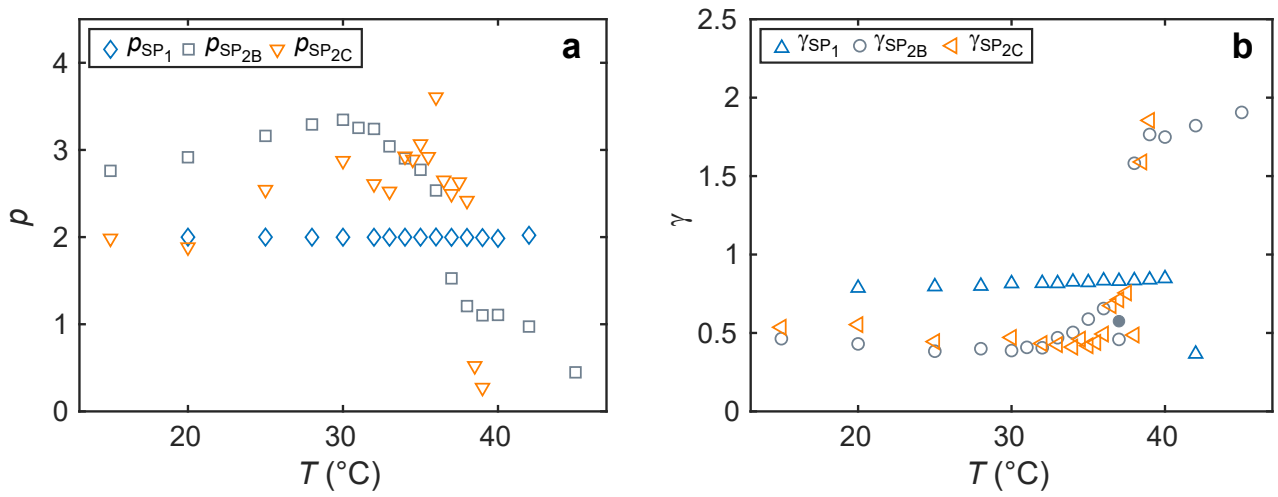


**Fig. 4** Temperature-dependency of a) $p$ (extracted from $\tau_c \propto q^p$) and b) KWW exponent $\gamma$, both shown for $SP_1$ at $\Phi_{\text{eff},20} = 0.14$, $SP_{2B}$ at $\Phi_{\text{eff},20} = 0.55$ and $SP_{2C}$ at $\Phi_{\text{eff},20} = 0.73$. Sample $SP_{2B}$ showed two relaxation processes at $37°$C, indicated by $\circ\ \gamma_1$/$\bullet\ \gamma_2$.

## Notes and references


1 L. Frenzel, F. Lehmkühler, I. Lokteva, S. Narayanan, M. Sprung and G. Grübel, *J. Phys. Chem. Lett.*, 2019, 5231–5236.

2 F. Lehmkühler, J. Valerio, D. Sheyfer, W. Roseker, M. A. Schroer, B. Fischer, K. Tono, M. Yabashi, T. Ishikawa and G. Grübel, *IUCrJ*, 2018, **5**, 801–807.

3 M. J. Bergman, N. Gnan, M. Obiols-Rabasa, J.-M. Meijer, L. Rovigatti, E. Zaccarelli and P. Schurtenberger, *Nat. Commun.*, 2018, **9**, 5039.

4 P. S. Mohanty, S. Nöjd, K. van Gruijthuijsen, J. J. Crassous, M. Obiols-Rabasa, R. Schweins, A. Stradner and P. Schurtenberger, *Sci. Rep.*, 2017, **7**, 1487.