

Solvent Mediated Assembly of Nanoparticles Confined in Mesoporous Alumina

K. J. Alvine,¹ D. Pontoni,¹ O. G. Shpyrko,^{1,2} P. S. Pershan,^{1,3} D. J. Cookson,⁴ K. Shin,⁵ T. P. Russell,⁵ M. Brunnbauer,⁶ F. Stellacci,⁶ & O. Gang⁷

¹DEAS, Harvard University; ²Center for Nanoscale Materials, Argonne National Laboratory; ³Department of Physics, Harvard University; ⁴ASRP, Argonne National Laboratory; ⁵Department of Polymer Science and Engineering, University of Massachusetts, Amherst; ⁶Department of Materials Science and Engineering, MIT; ⁷Center for Functional Nanomaterials, Brookhaven National Lab

Abstract

In-situ small angle x-ray scattering measurements of the solvent mediated assembly of 2 nm diameter Au-core colloidal nanoparticles inside mesoporous alumina are presented. The evolution of the self-assembly process was controlled reversibly via solvent condensed from vapor. Measurements of the absorption & desorption of solvent showed strong hysteresis upon thermal cycling. In addition, the capillary transition for the solvent in the nanoparticle-doped pores was shifted to greater under-saturation by a factor of four relative to the expected value for the same system sans nanoparticles. Analysis indicated that a cylindrical shell super-structure of the nanoparticles is maintained throughout the addition and removal of liquid solvent. Nanoparticle nearest-neighbor separation increased and the in-shell order decreased with the addition of solvent. The process was reversible with the removal of liquid. Isotropic clusters of nanoparticles were also observed to form temporarily during desorption of the liquid solvent and disappear upon complete removal of liquid.

Motivation

- Understanding self-assembly of nanoparticles important for both fundamental physics and technological viewpoints.
- Applications: magnetic storage, catalysis, electro-optical devices, etc.
- Quasi-1D systems of particular interest: nanowires, similarity with biological systems such as some virus protein coatings and cell microtubules.
- Some experiments on end product in cylindrical geometry, no *in-situ*!
- There have been several experiments of nanoparticle self-assembly on flat substrates using bulk methods, i.e. droplet evaporation.
- These methods not possible for ~1D systems which require templates.
- Need reversible, method for condensing liquid into the system
- This is achieved via our ΔT method to sub-nm film thickness!
- Need nondestructive, non-invasive, *in-situ* method for measuring the evolution of the nanoparticle evolution as function of condensation
- Small Angle X-Ray scattering perfect for this investigation!

Experimental

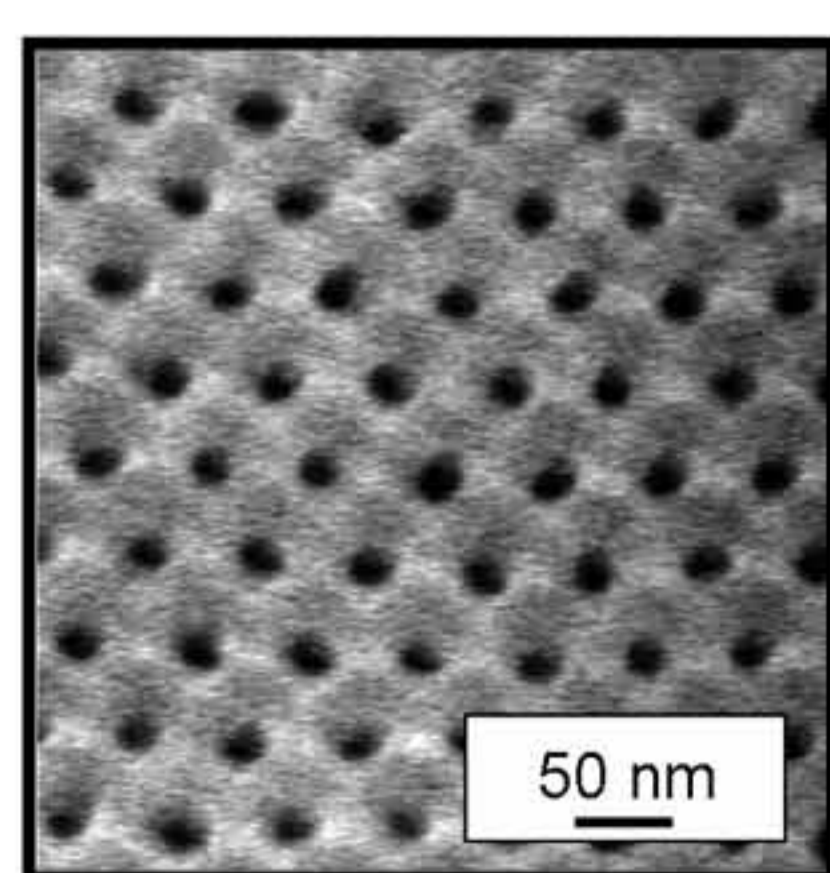


Figure 1a: (Left) SEM image shows well ordered 2D hexagonal packing of alumina nanopores prepared under similar conditions to samples used for x-ray experiments.

Figure 1b: (Right) Bright-field TEM image of the nanoparticles (arrow) on the walls (faint diagonal lines) of alumina pores. The nanoparticles are Au-core with octane-thiol coating. Cross-sections of the hybrid samples were prepared by the ultramicrotome method from the sample used for x-ray experiments.

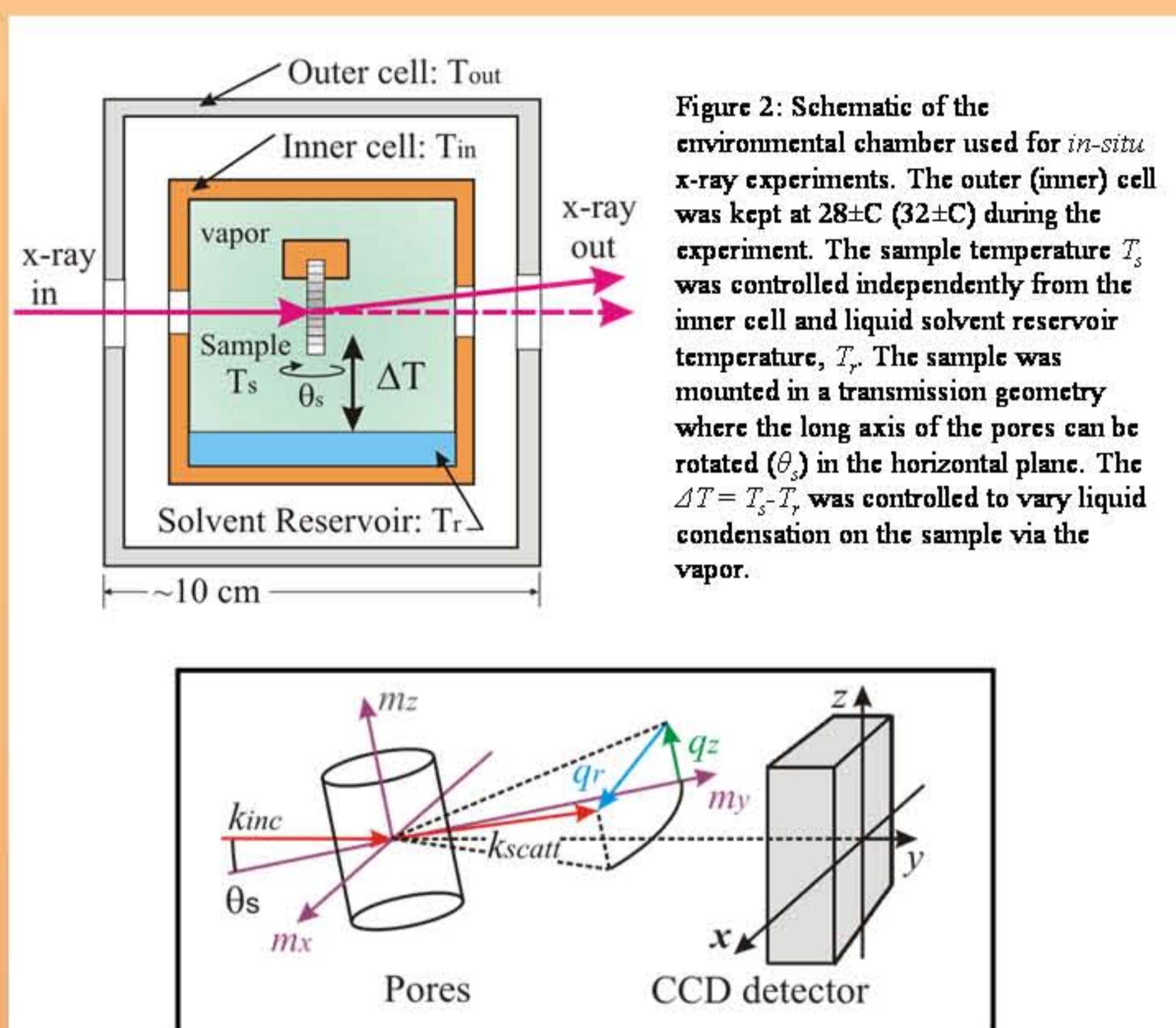
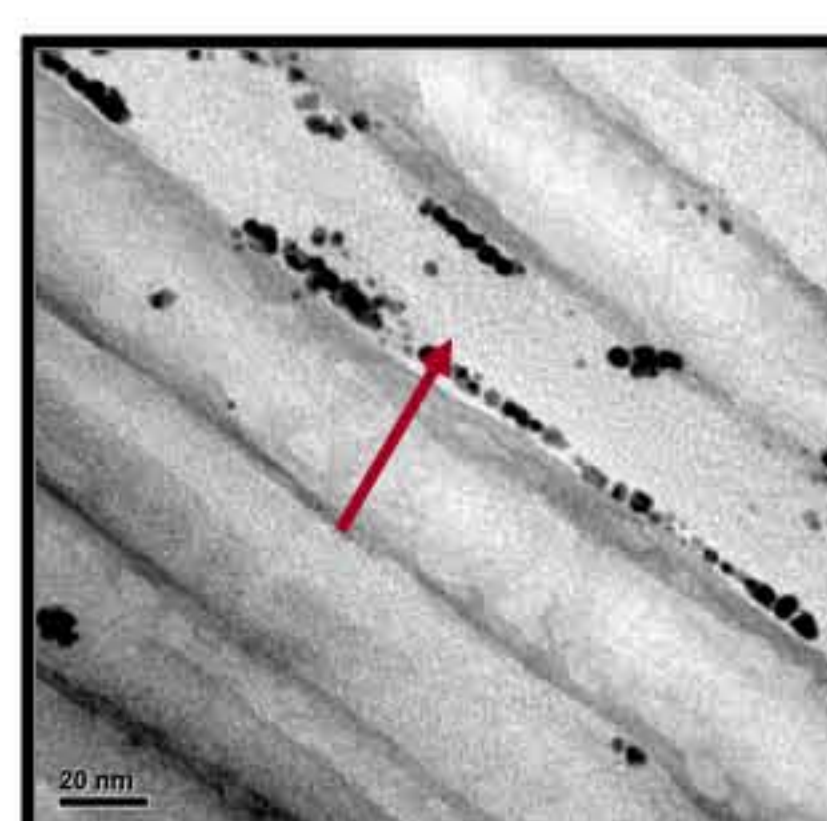


Figure 2: Schematic of the environmental chamber used for *in-situ* x-ray experiments. The outer (inner) cell was kept at 28±C (32±C) during the experiment. The sample temperature T_s was controlled independently from the inner cell and liquid solvent reservoir temperature, T_r . The sample was mounted in a transmission geometry where the long axis of the pores can be rotated (θ_s) in the horizontal plane. The $\Delta T = T_r - T_s$ was controlled to vary liquid condensation on the sample via the vapor.

Results

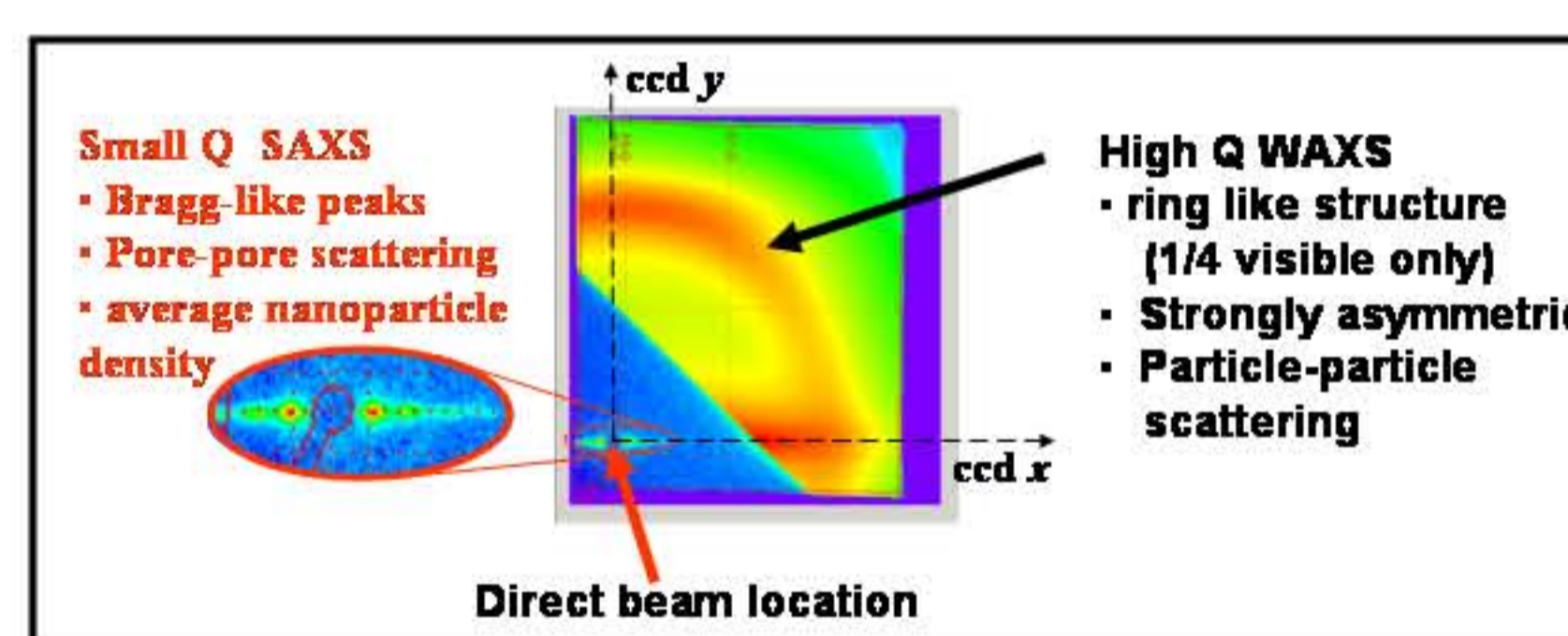


Figure 4: Typical CCD image of scattering intensity. Two different scattering regimes were observed: intense small angle powder diffraction peaks due to the 2D ordering of the nanopores and at higher angles or (WAXS) a broader, weak anisotropic ring from the local nanoparticle packing. The dark blue region in the lower left corner is due to an attenuator.

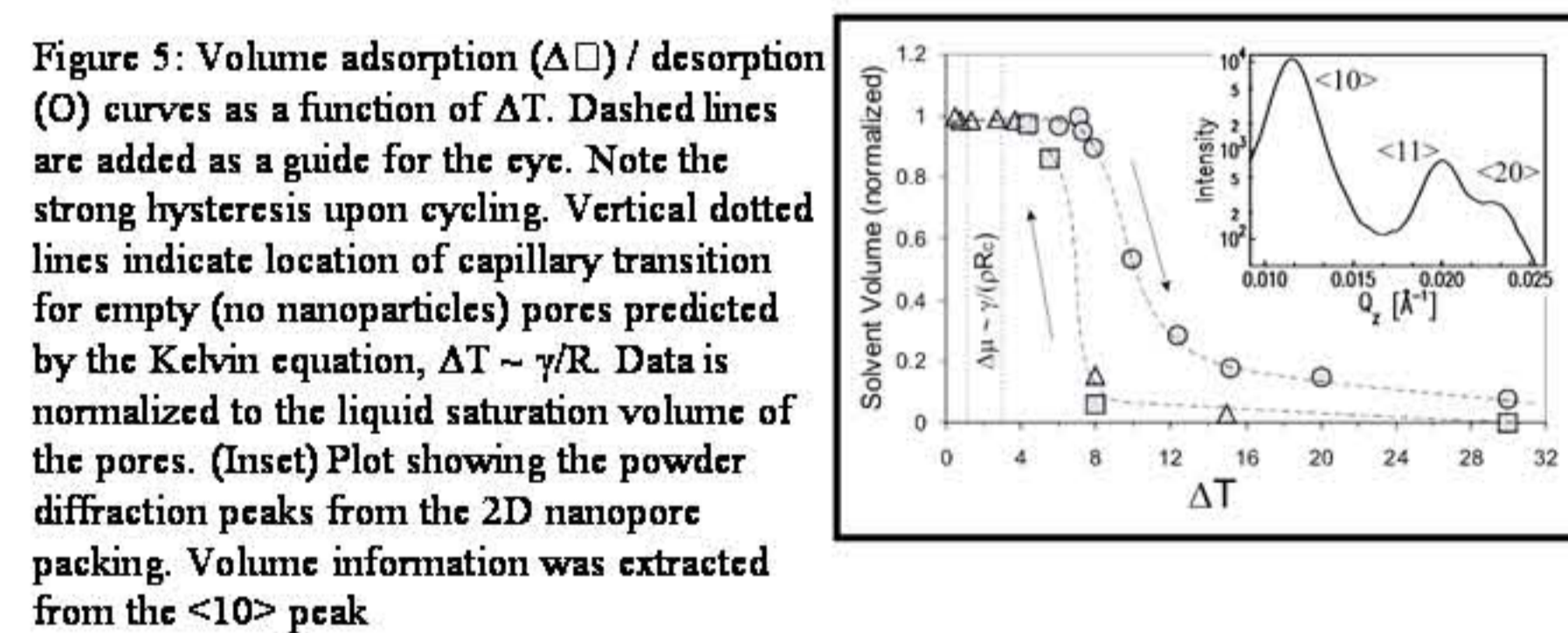


Figure 5: Volume adsorption (Δ) / desorption (O) curves as a function of ΔT . Dashed lines are added as a guide for the eye. Note the strong hysteresis upon cycling. Vertical dotted lines indicate location of capillary transition for empty (no nanoparticles) pores predicted by the Kelvin equation, $\Delta T \sim \gamma/R$. Data is normalized to the liquid saturation volume of the pores. (Inset) Plot showing the powder diffraction peaks from the 2D nanopore packing. Volume information was extracted from the $\langle 10 \rangle$ peak.

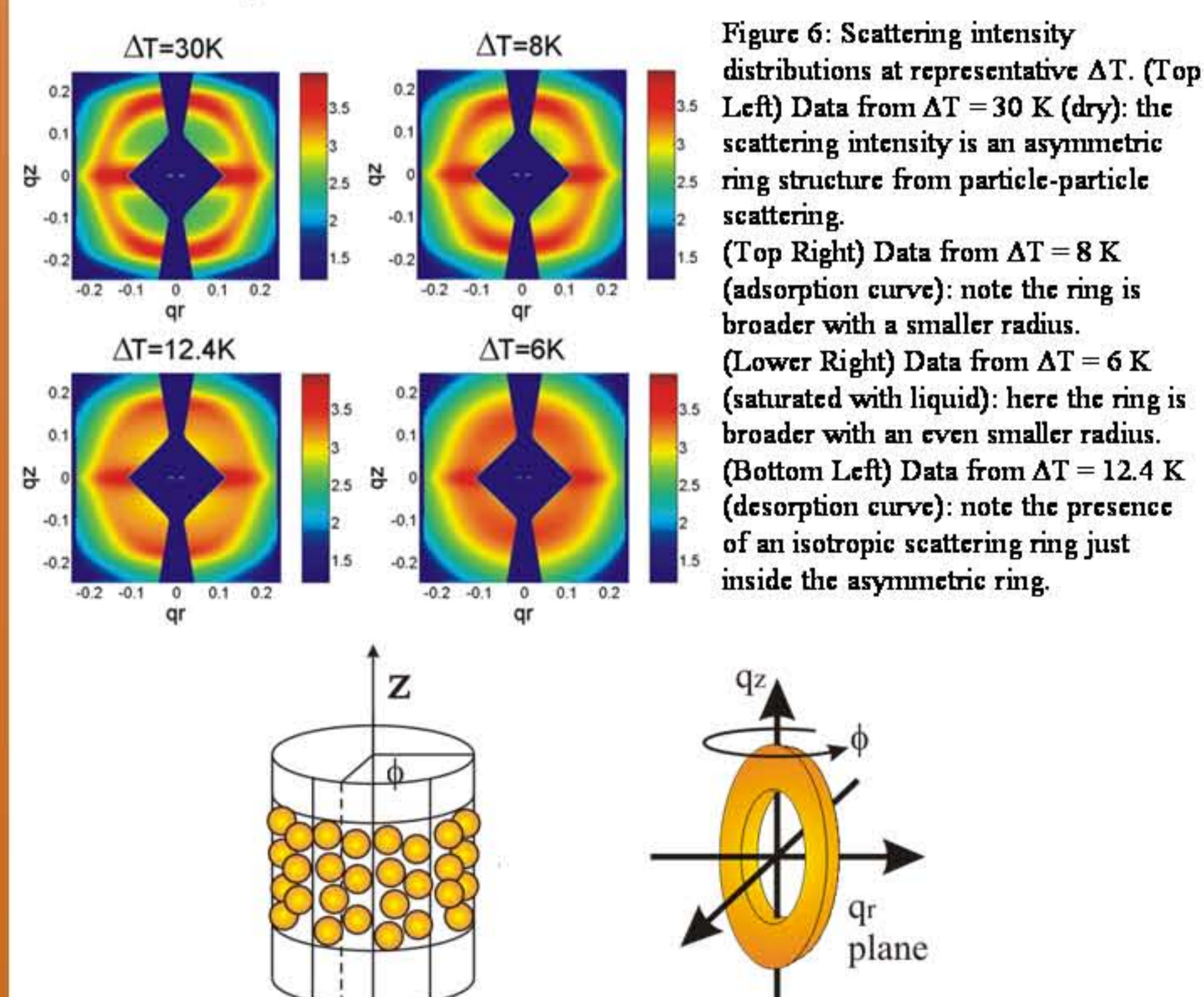


Figure 6: Scattering intensity distributions at representative ΔT . (Top Left) Data from $\Delta T = 30$ K (dry): the scattering intensity is an asymmetric ring structure from particle-particle scattering. (Top Right) Data from $\Delta T = 8$ K (adsorption curve): note the ring is broader with a smaller radius. (Lower Right) Data from $\Delta T = 6$ K (saturated with liquid): here the ring is broader with an even smaller radius. (Bottom Left) Data from $\Delta T = 12.4$ K (desorption curve): note the presence of an isotropic scattering ring just inside the asymmetric ring.

Figure 7: To model the scattering a monolayer of nanoparticles around the pore wall is assumed. The monolayer is broken into nearly flat tiles and powder averaged over all tiles from all pores at a given ϕ . This scattering can be modeled with a 2D Lorentzian ring x form factor for the nanoparticles. The total scattering is given by the integration over all ϕ .

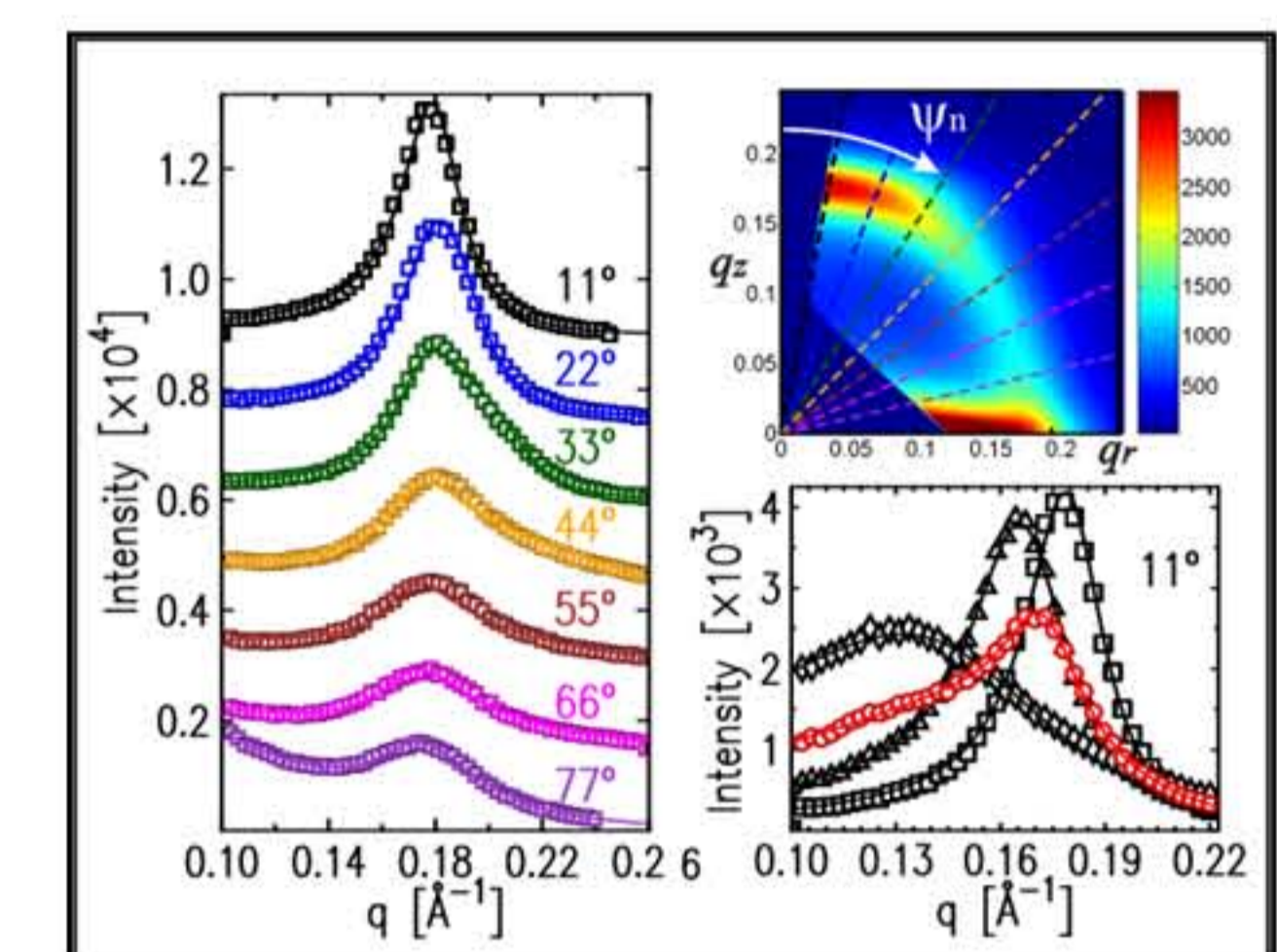


Figure 8: (Right Top) Schematic of representative radial slices (dashed lines) taken for fitting with the tile model with $\Psi_n = 11 X n$, n an integer from 1 to 7. (Left) Data (\square) at $\Delta T = 30$ K from each slice (color coded with dashed lines) along with fits (solid lines) from the tile model plus independent monotonically decaying, positive backgrounds. Error bars are smaller than data symbols. (Bottom Right) Data (all at $\Psi_n = 11$) from four different ΔT : $\square = 30$ K, $\Delta = 8$ K (adsorption), $\circ = 4.4$ K (saturated), and $\circ = 12.4$ K (desorption); solid lines are fits. Note that $\Delta T = 12.4$ K is qualitatively different and requires an isotropic component in addition to the tile model to fit properly.

Figure 9: Illustration of a possible mechanism for creation of isotropic clusters of particles upon desorption. Right, pores fill by cylindrical film growth, empty by hemispherical menisci from the ends (Cohan mechanism). These menisci may drag particles along, creating clusters temporarily as the solvent is removed from the pores.

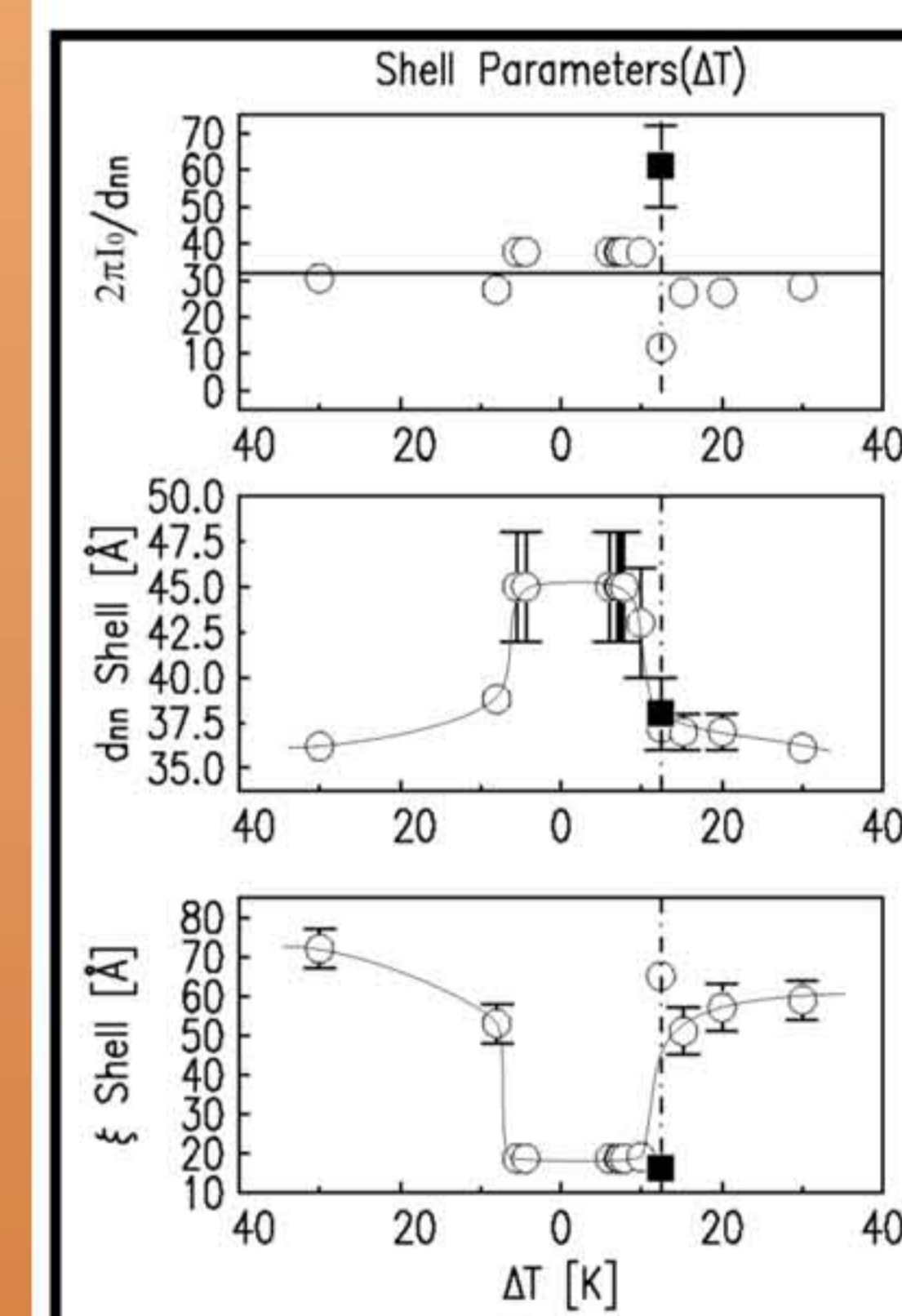
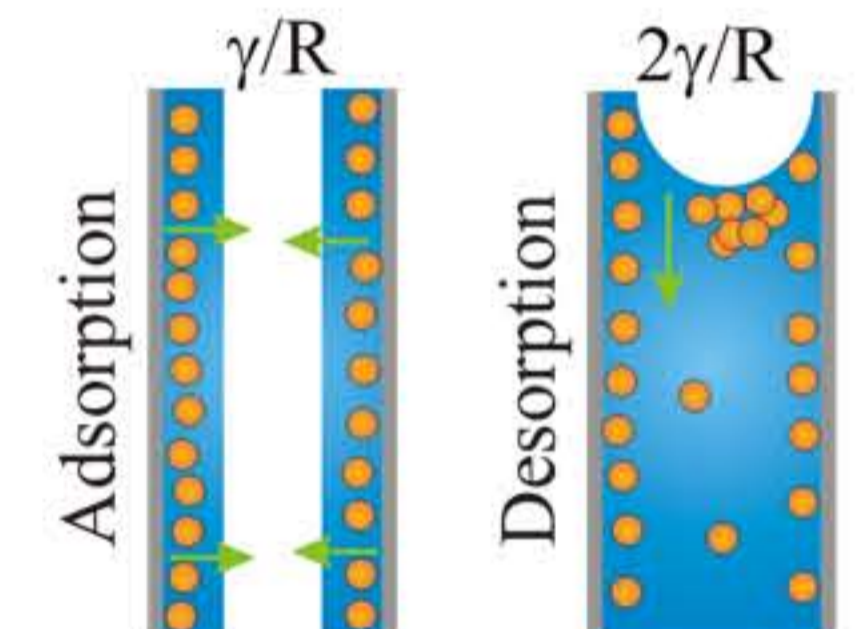


Figure 10: Plots of the "best fit" tile model (O) and isotropic (■) parameters and uncertainties as a function of ΔT (data to the left of zero are from adsorption curves, to the right are from desorption curves). The physical parameters are (top to bottom): number of scatters $\sim \lg d_{300}$, nearest neighbor spacing d_{300} , and order parameter ξ . Lines are added as a guide to the eye.

Conclusions

Solvent Mediated Self-Assembly in pores

- Shift in capillary transition due to nanoparticles, strong hysteresis
 - Suggests Cohan mechanism
 - May explain clusters as well
- Dry case: nanoparticle monolayer.
- Add Solvent: particle separation increases, ordering decreases
- Remove Solvent: particle separation decreases, ordering increases
 - Additionally evidence for isotropic particle clusters is observed.

Acknowledgements

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