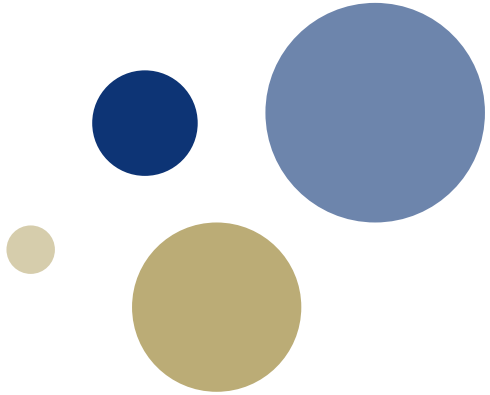
NTNU – Trondheim
Norwegian University of
Science and Technology



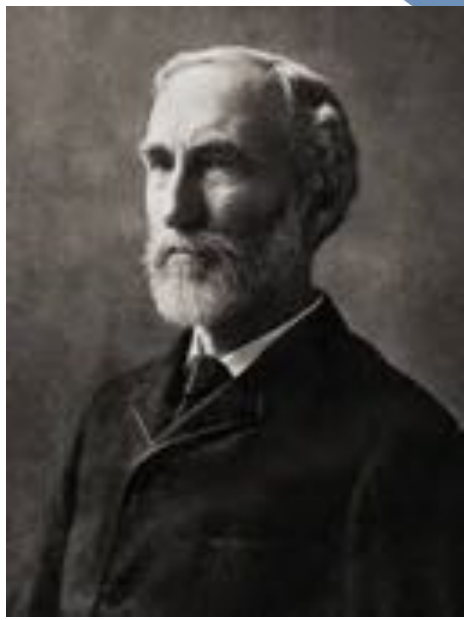
Nanothermodynamics to bridge nano and mesoscopic scales

Sondre K. Schnell
Department of Materials Science and Engineering
Faculty of Natural Science
NTNU

Outline

- Thermodynamics and small systems
- Small system method
- Sampling from MD trajectories
- What to calculate
- Systems of interest

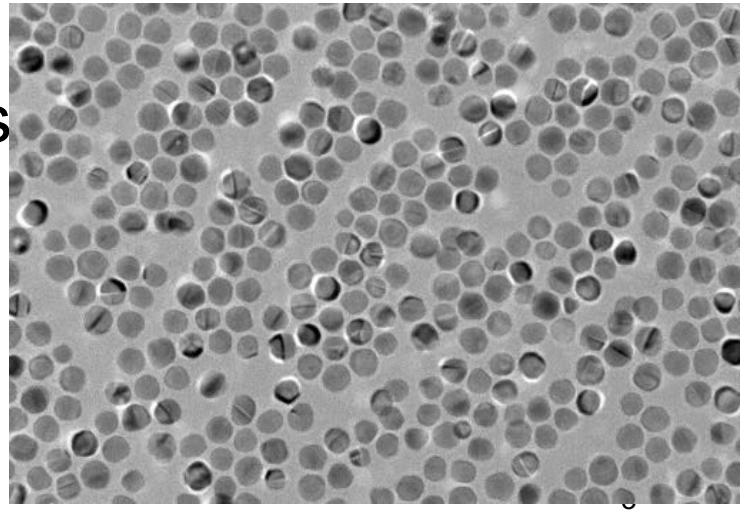
Thermodynamics



- Thermodynamics is for ”large” systems
  - 10^{23} atoms ++

- Smaller and smaller systems

- Thermodynamics for “small” systems



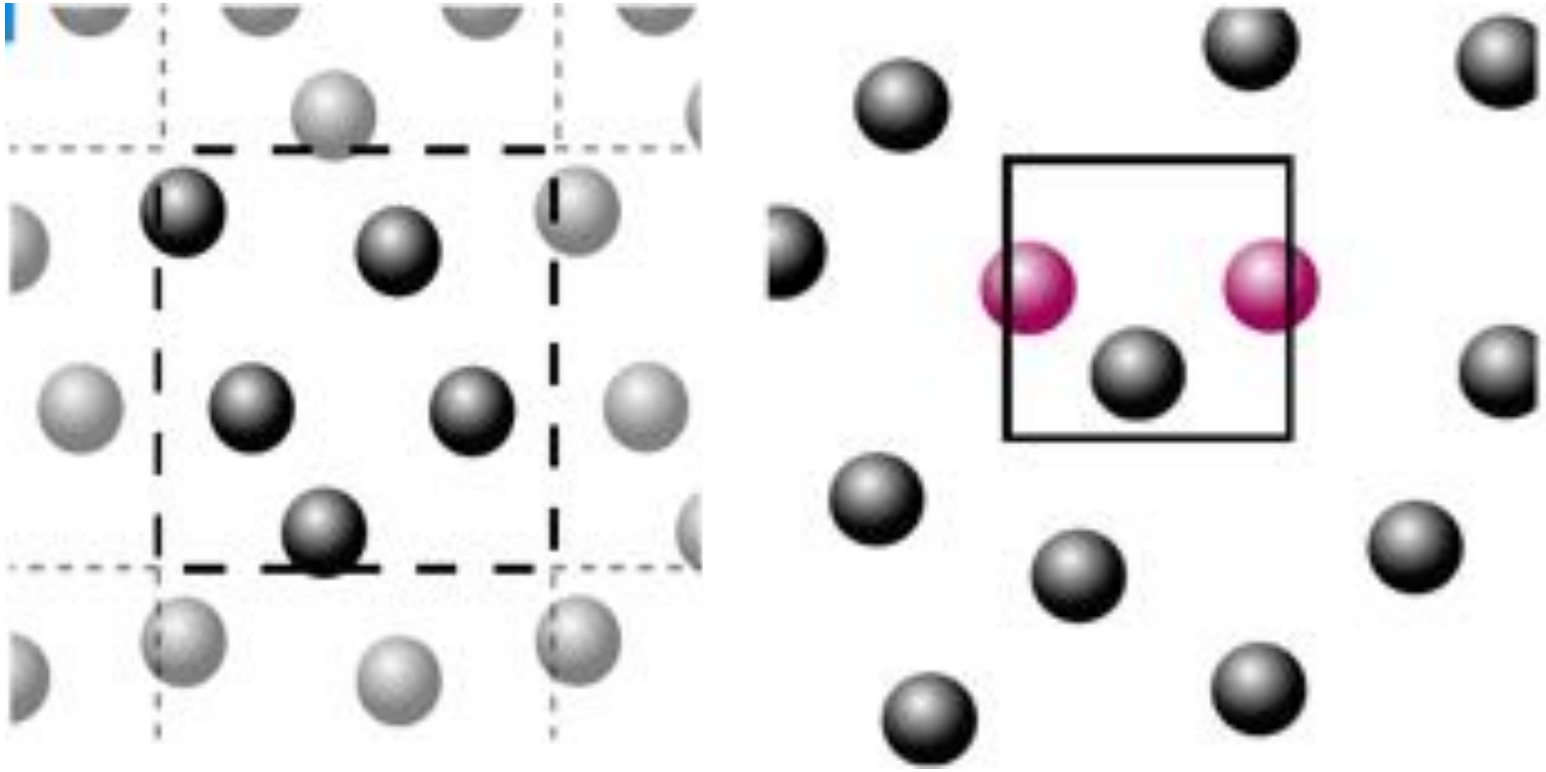
Hill's thermodynamics

- "Nanothermodynamics" or "thermodynamics of small systems"

- $dU_t = TdS_t - pdV + \mu dV_t + \varepsilon dN$

- Divides the system in *N* clusters
- ε is a sub-division potential
- "Correction" due to small size

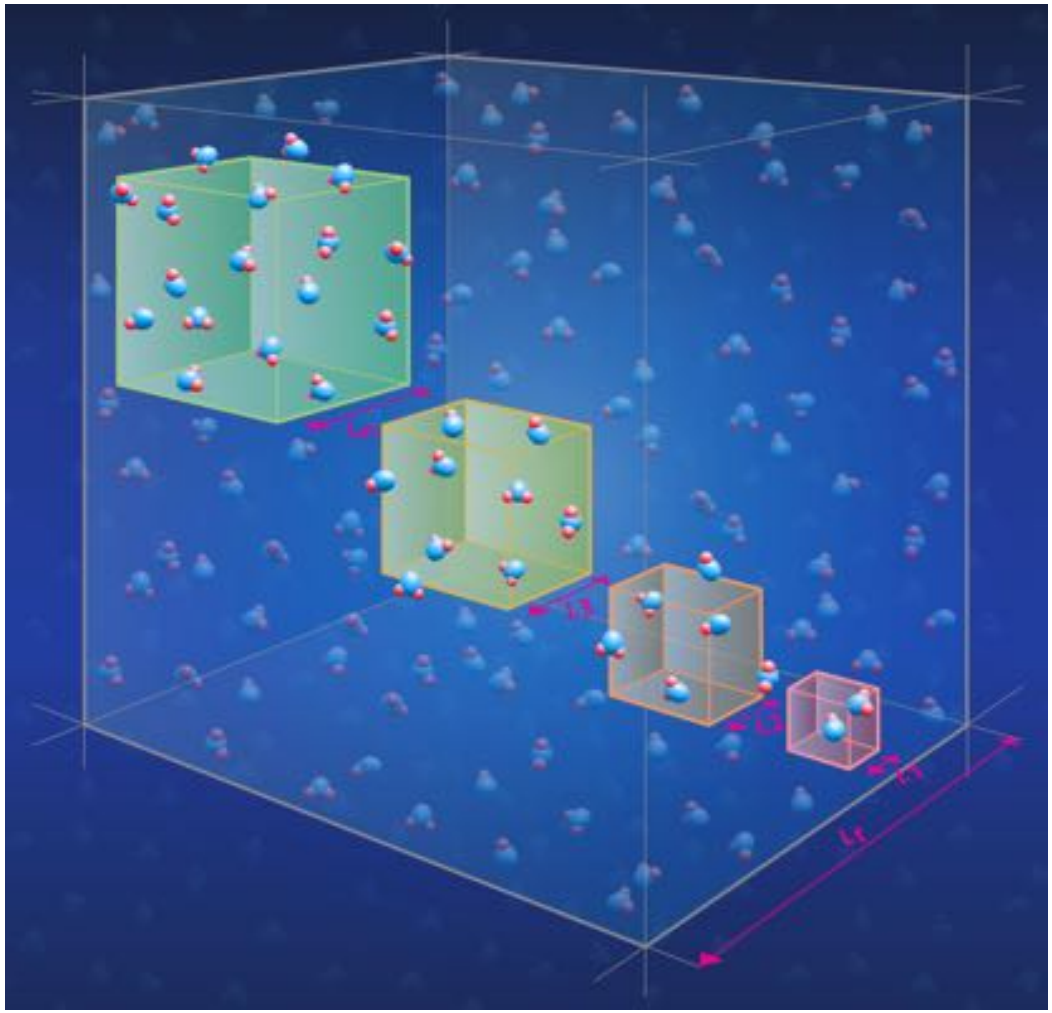
Small system method



- Creating a small ”cut-out” from a system makes it deviate from a periodic system

Scaling

- Scaling
- Systematically changing the size
- Properties from the small systems calculated for each size



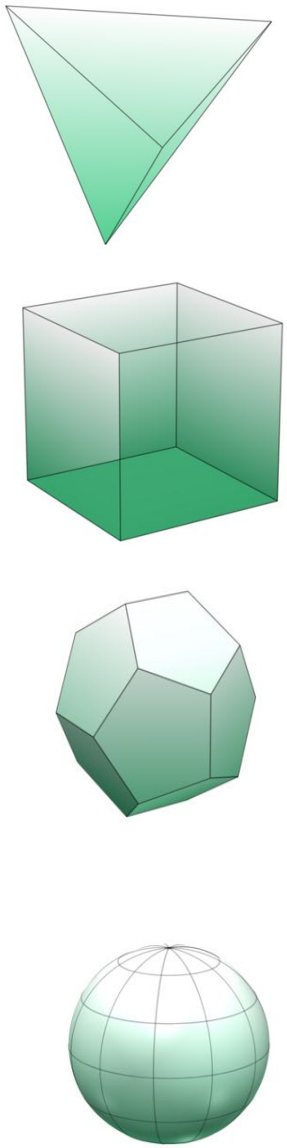
Fluctuations

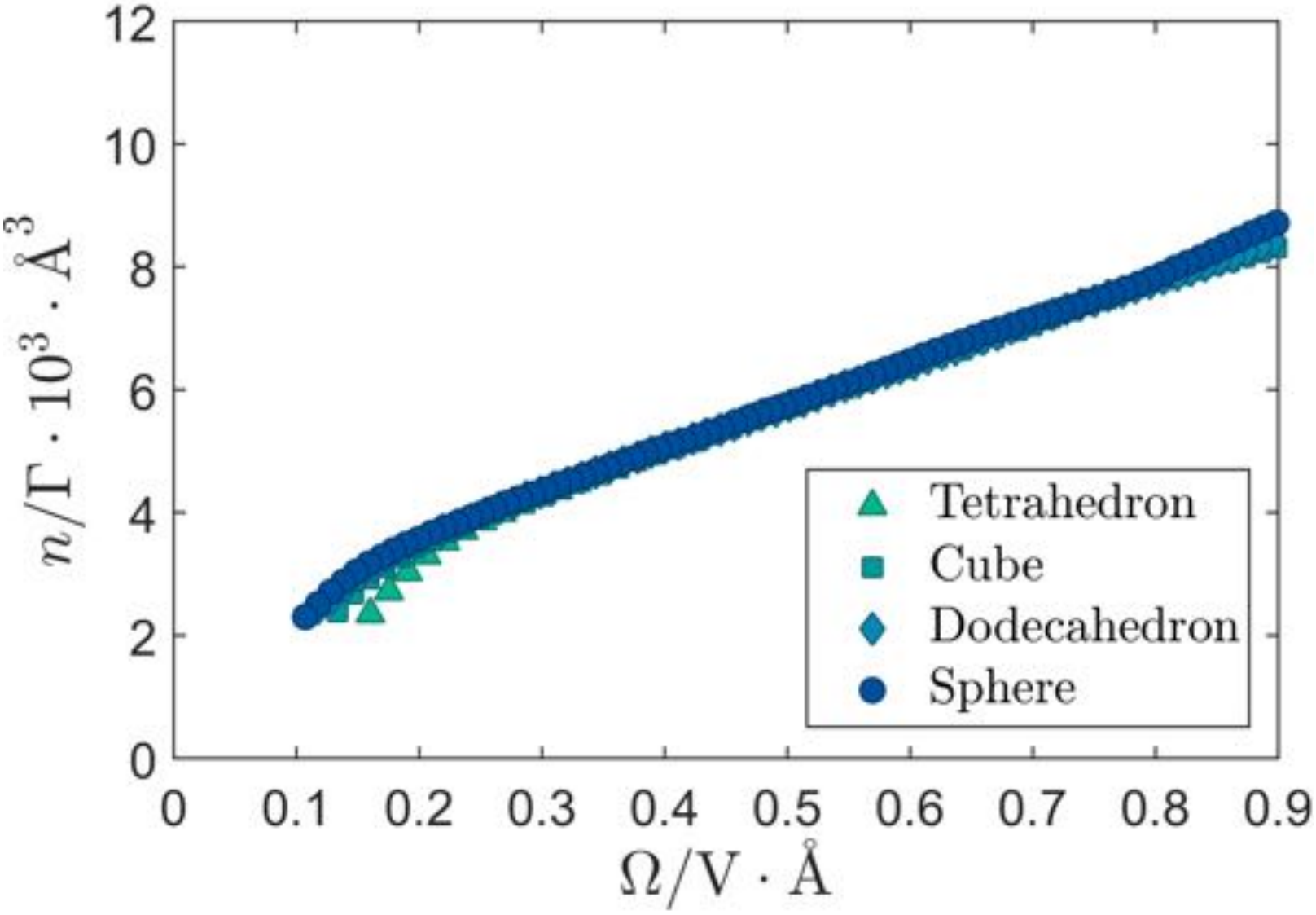
- $\frac{1}{\Gamma} = k_B T \left(\frac{\partial \ln \bar{N}}{\partial \mu}\right)_{T,V} = \frac{\langle N^2 \rangle - \langle N \rangle^2}{\langle N \rangle}$

- $\left(\frac{\partial \hat{H}}{\partial \bar{N}_i}\right)_{T,V,\mu} = \frac{\overline{UN_i} - \bar{U}\overline{N_i} + \overline{N_i} k_B T}{\overline{N_i^2} - \overline{N_i}^2}$

- $G_{\alpha\beta} = V \frac{\langle N_\alpha N_\beta \rangle - \langle N_\alpha \rangle \langle N_\beta \rangle}{\langle N_\alpha \rangle \langle N_\beta \rangle} - \frac{\delta_{\alpha\beta}}{c_\alpha} =$
  $4\pi \int_0^\infty \left[g_{\alpha\beta}^{\mu VT}(r) - 1 \right] r^2 dr \approx$
  $4\pi \int_0^R \left[g_{\alpha\beta}^{NVT}(r) - 1 \right] r^2 dr$

Thermodynamic factors

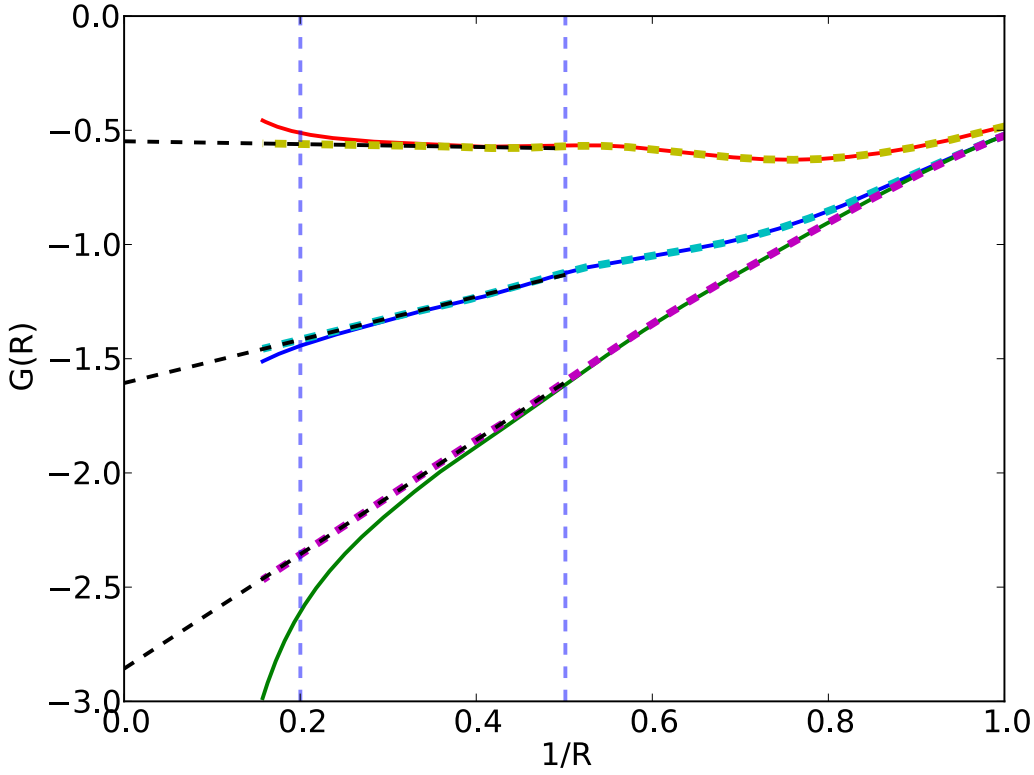




Kirkwood-Buff theory

$$G^V_{\alpha\beta} \equiv \frac{1}{V}\int_V \int_V (g_{\alpha\beta}(r_{12}) - 1)\mathrm{d}\mathbf{r}_1\mathrm{d}\mathbf{r}_2$$

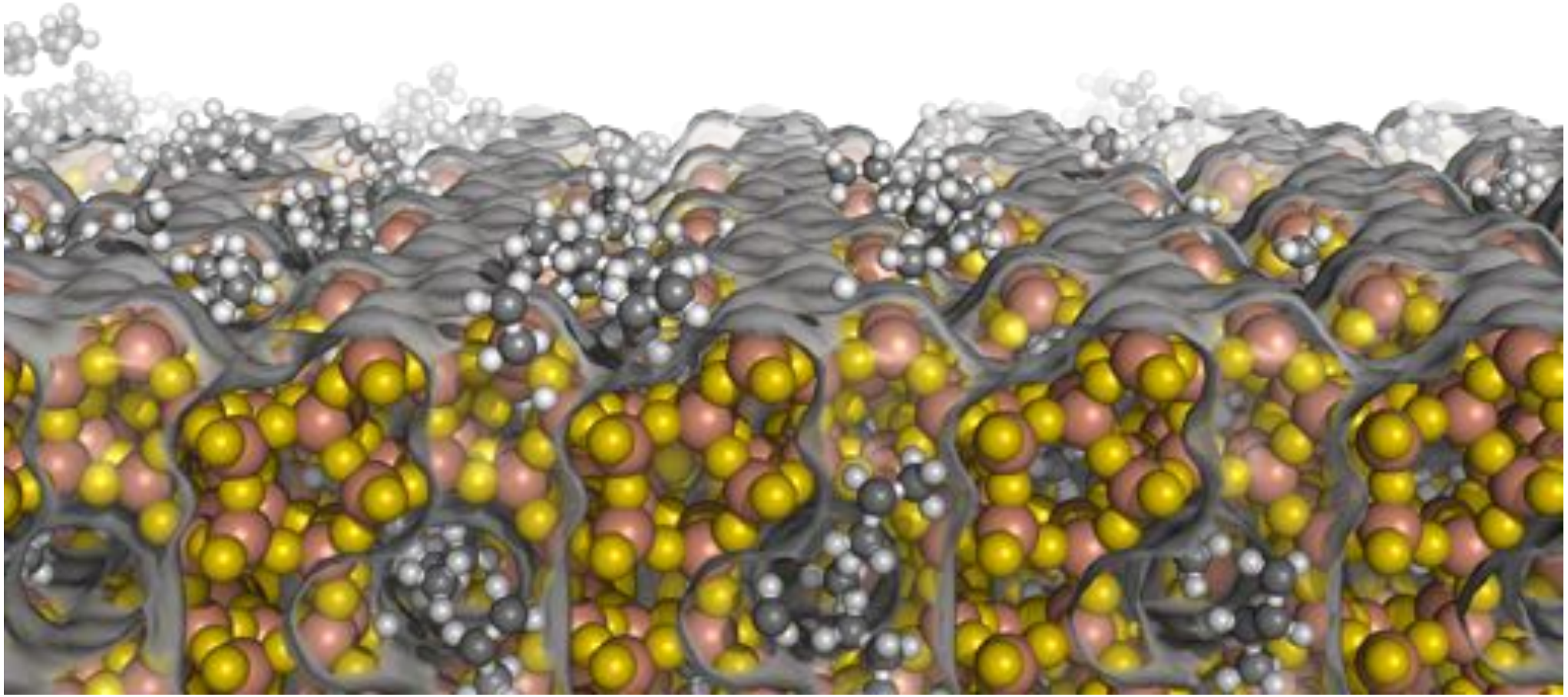
$$= 4\pi \int_0^{2R} (g_{\alpha\beta}(r) - 1)r^2\left(1 - \frac{3r}{4R} + \frac{r^3}{16R^3}\right)\mathrm{d}r \equiv G_{\alpha\beta}(R)$$



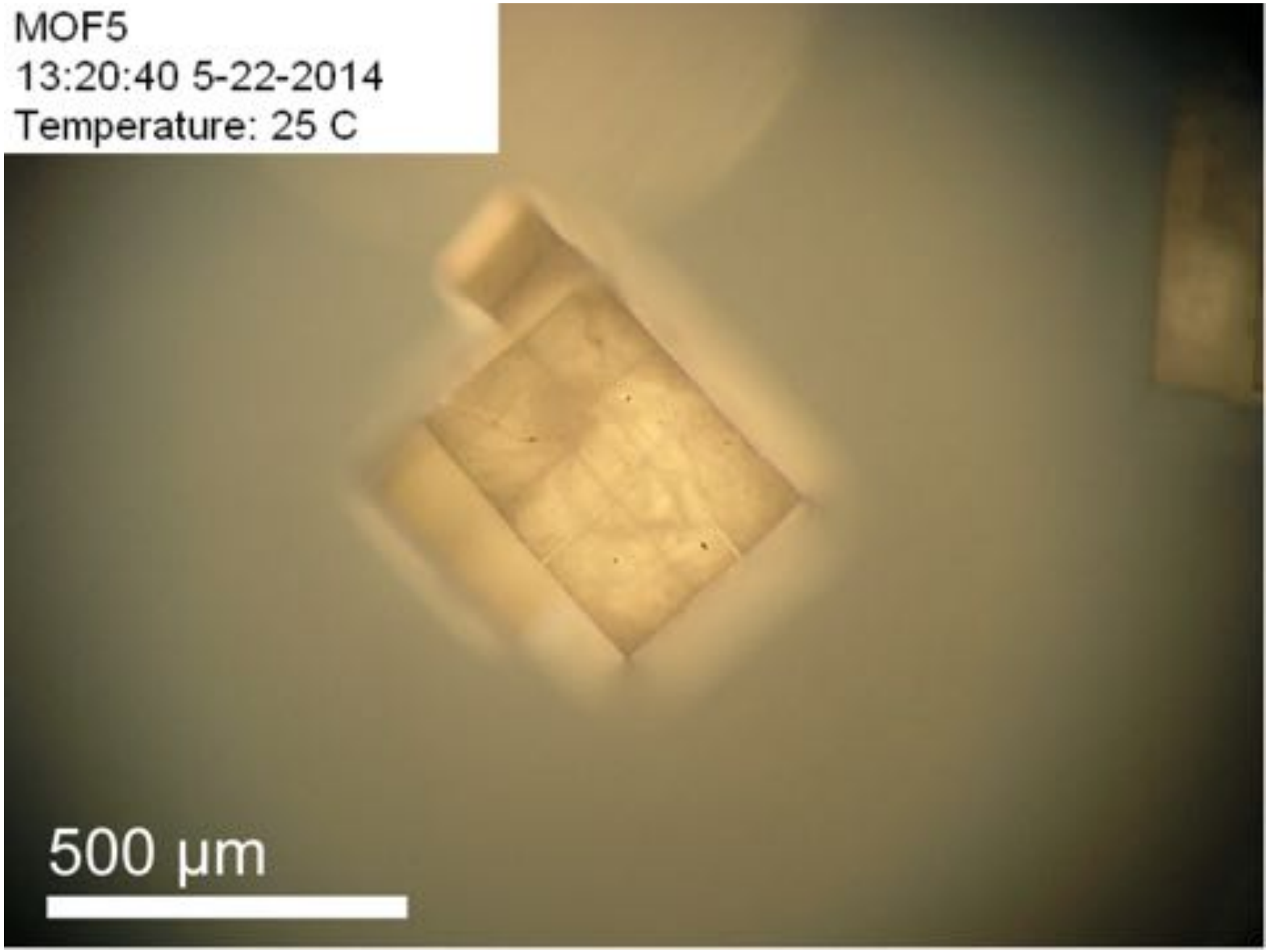
FUTURE WORK

Surface properties

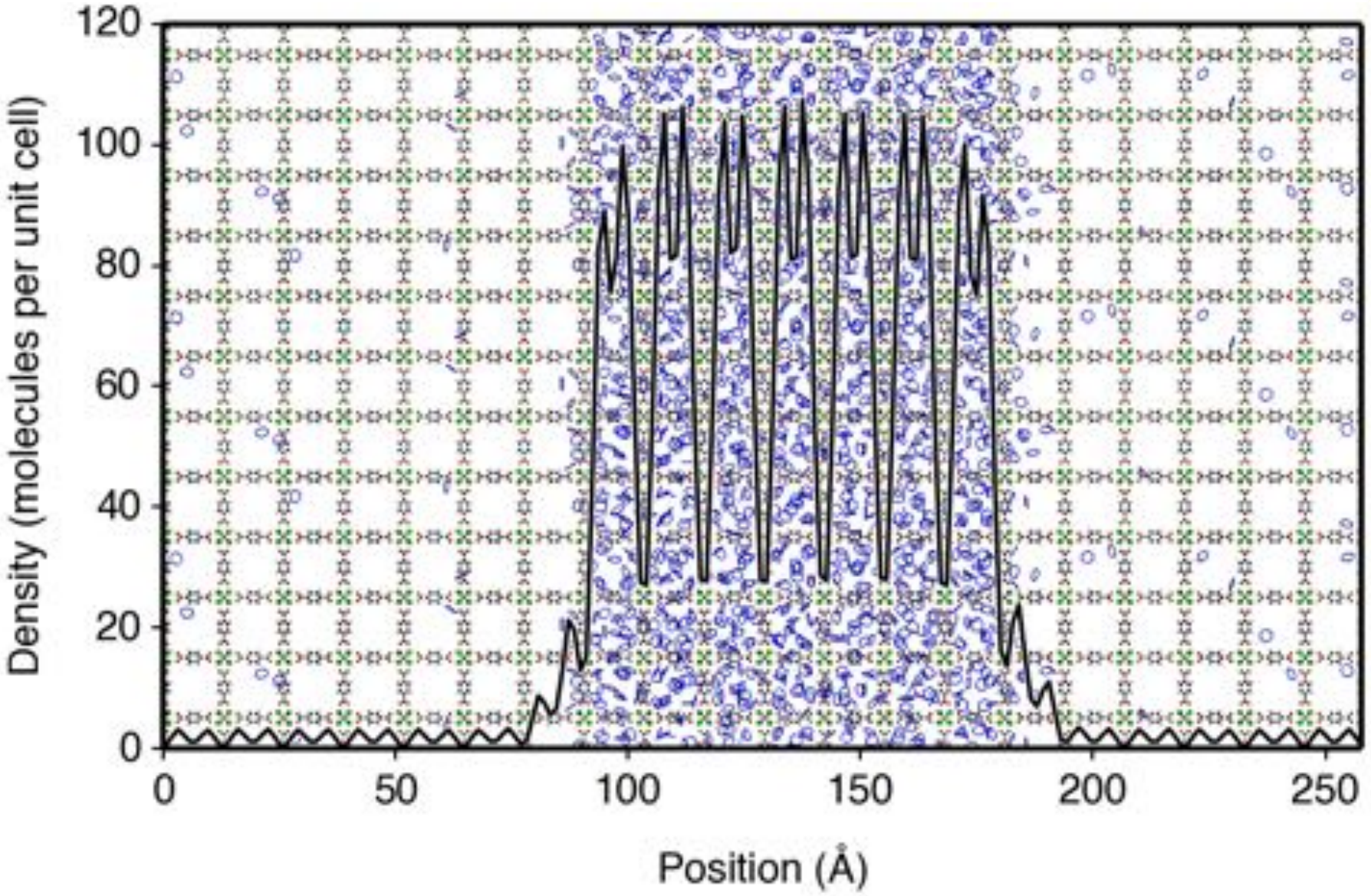
- Surfaces are thin → Small systems



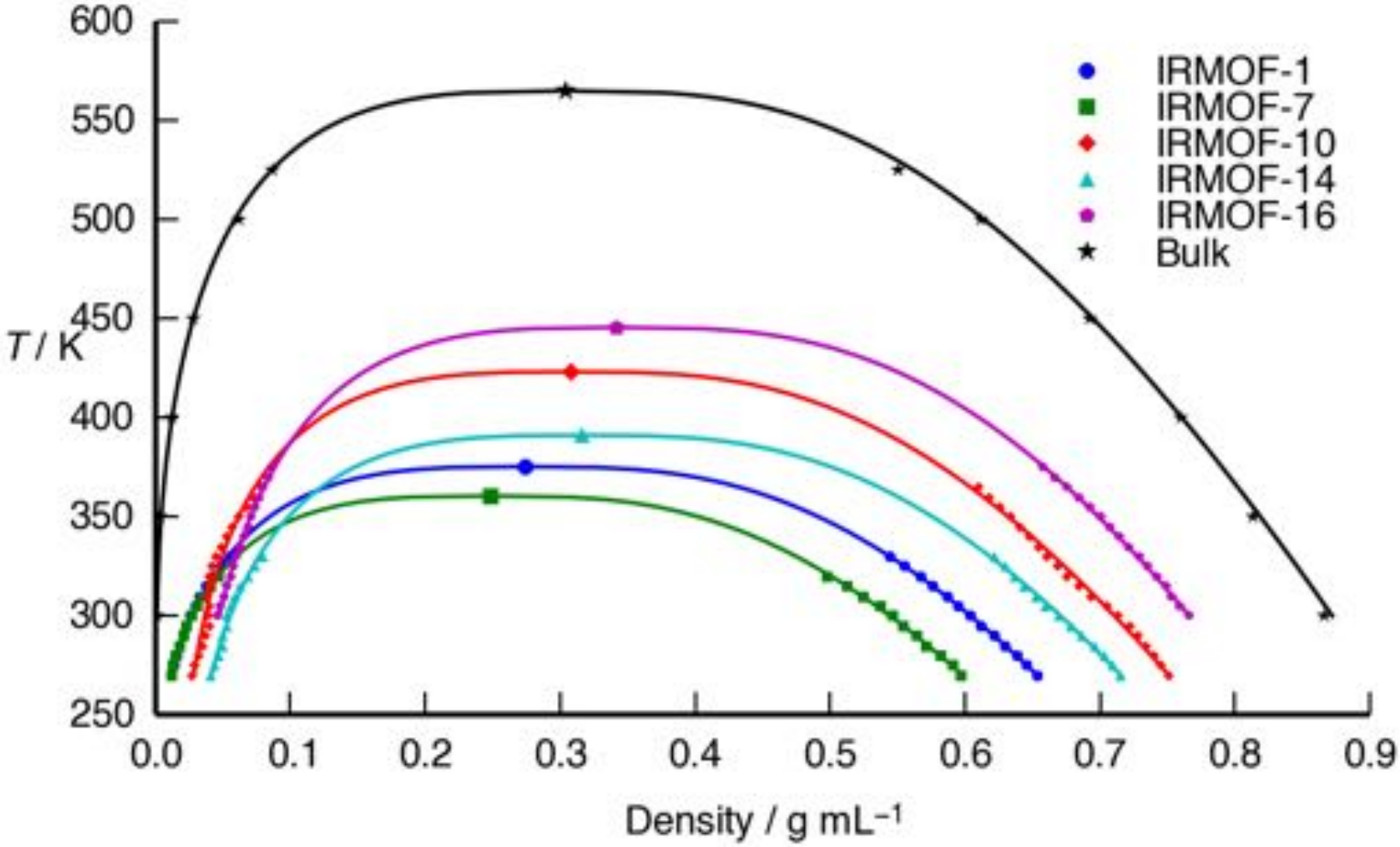
Porous materials – Anomalous diffusion behavior



Phase eq. in porous system



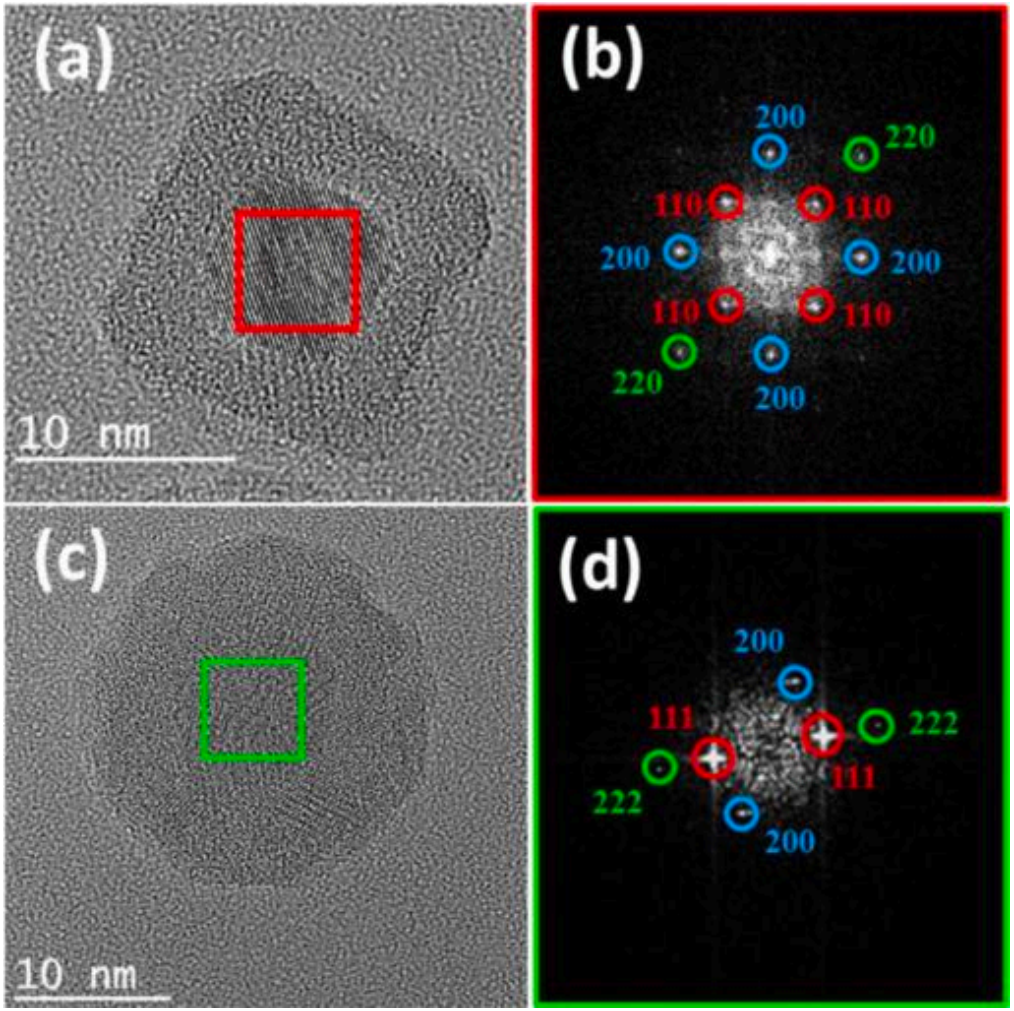
Modifies critical point



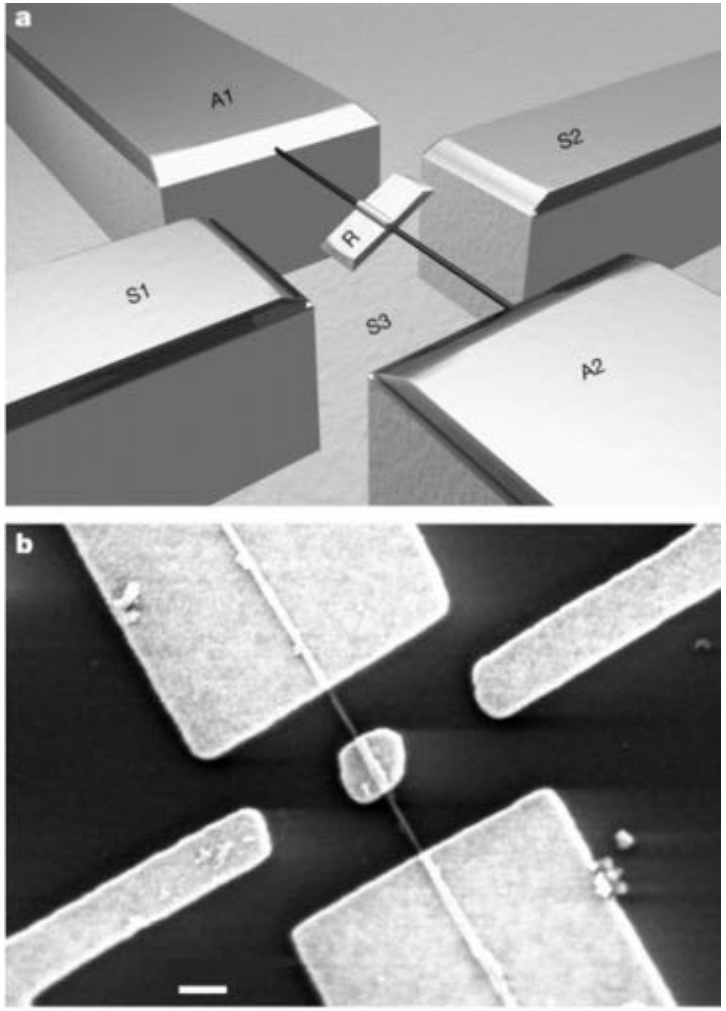
Small droplets

- The equilibrium can be found in different materials
- Pore diameter smaller then what is expected to give capillary condensation
- Liquid phase extends beyond unitcell-diameter
  - but are still limited in size

Understanding nanoparticles



Molecular machines



Conclusion

- Thermodynamics still valid, even to very small systems
- Can calculate properties in bulk from sampling small systems
- True handle on KB integrals
- Not really clear how to use for actual small systems yet, need experimental collaborator

Thanks to …

- Signe Kjelstrup
- Dick Bedeaux
- Jean-Marc Simon
- Thijs J. H. Vlugt
- Bjørn Strøm
- Efrem Braun
- Berend Smit