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2054-11

Structure and Dynamics of Hydrogen-Bonded Systems

26 - 27 October 2009

Is Water Homogeneous or Inhomogeneous?

Alan SOPER

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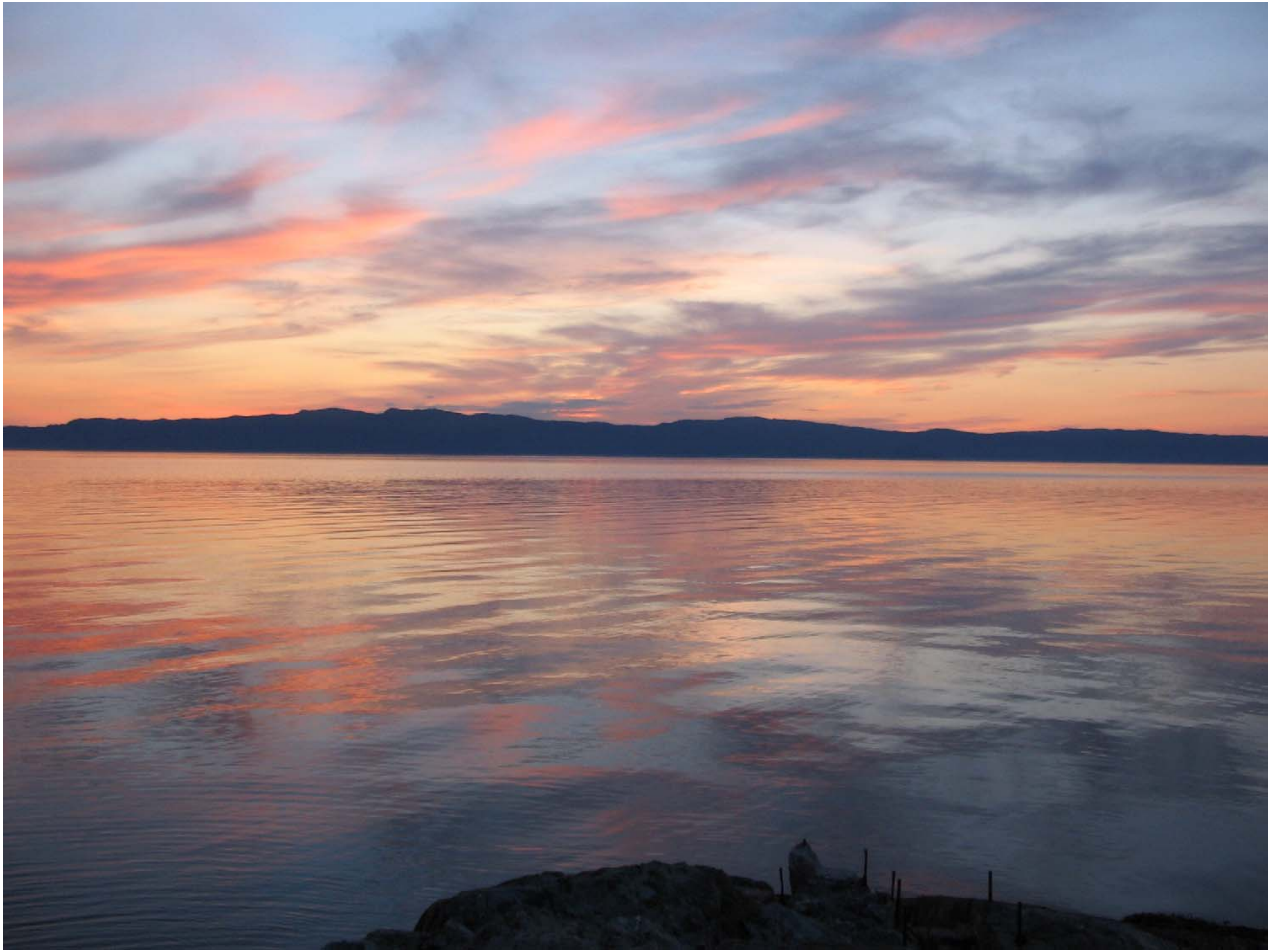

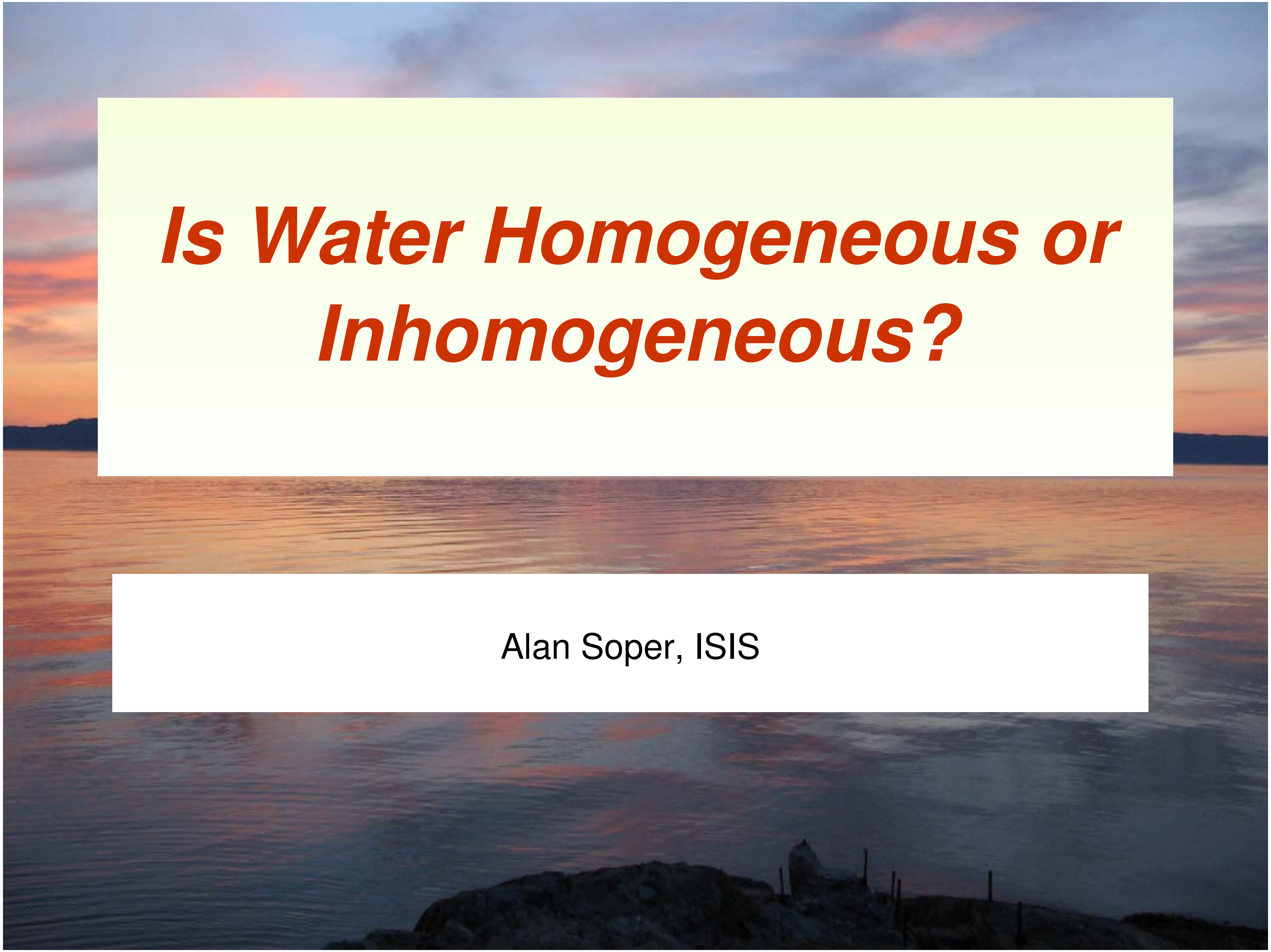

Is Water Homogeneous or Inhomogeneous?

Alan Soper, ISIS

PNAS

The inhomogeneous structure of water at ambient conditions

C. Huang[a], K. T. Wikfeldt[b], T. Tokushima[c], D. Nordlund[a], Y. Harada[c,d], U. Bergmann[a], M. Niebuhr[a], T. M. Weiss[a], Y. Horikawa[c,e], M. Leetmaa[b], M. P. Ljungberg[b], O. Takahashi[f], A. Lenz[g], L. Ojamäe[g], A. P. Lyubartsev[h], S. Shin[c,i], L. G. M. Pettersson[b], and A. Nilsson[a,b,1]

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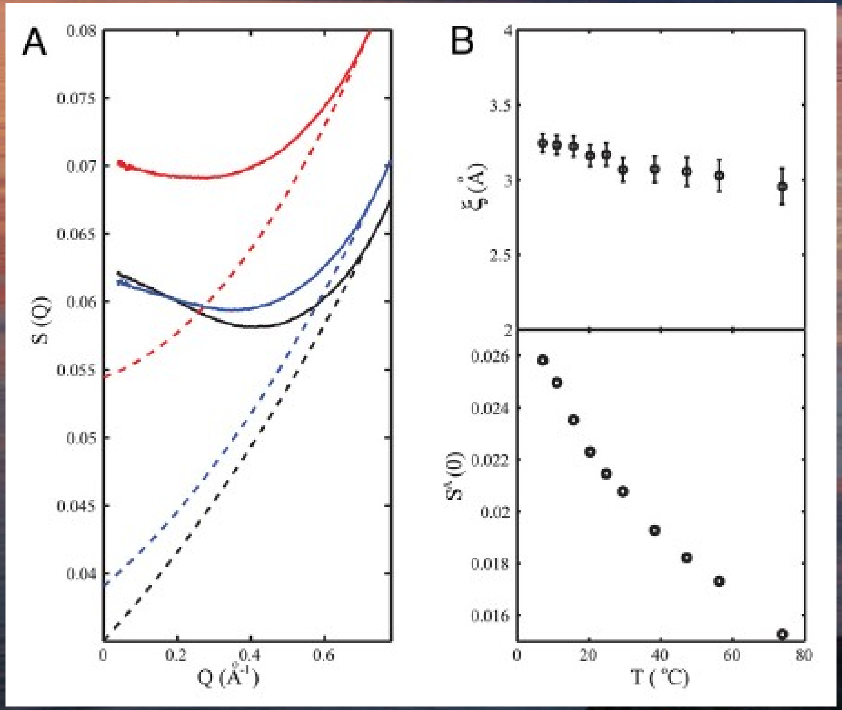
Edited by H. Eugene Stanley, Boston University, Boston, MA, and approved July 7, 2009 (received for review May 7, 2009)



"… Based on X-ray emission spectroscopy and X-ray Raman scattering data we propose that the density difference contrast in SAXS is due to fluctuations between tetrahedral-like and hydrogen-bond distorted structures related to, respectively, low and high density water. …"

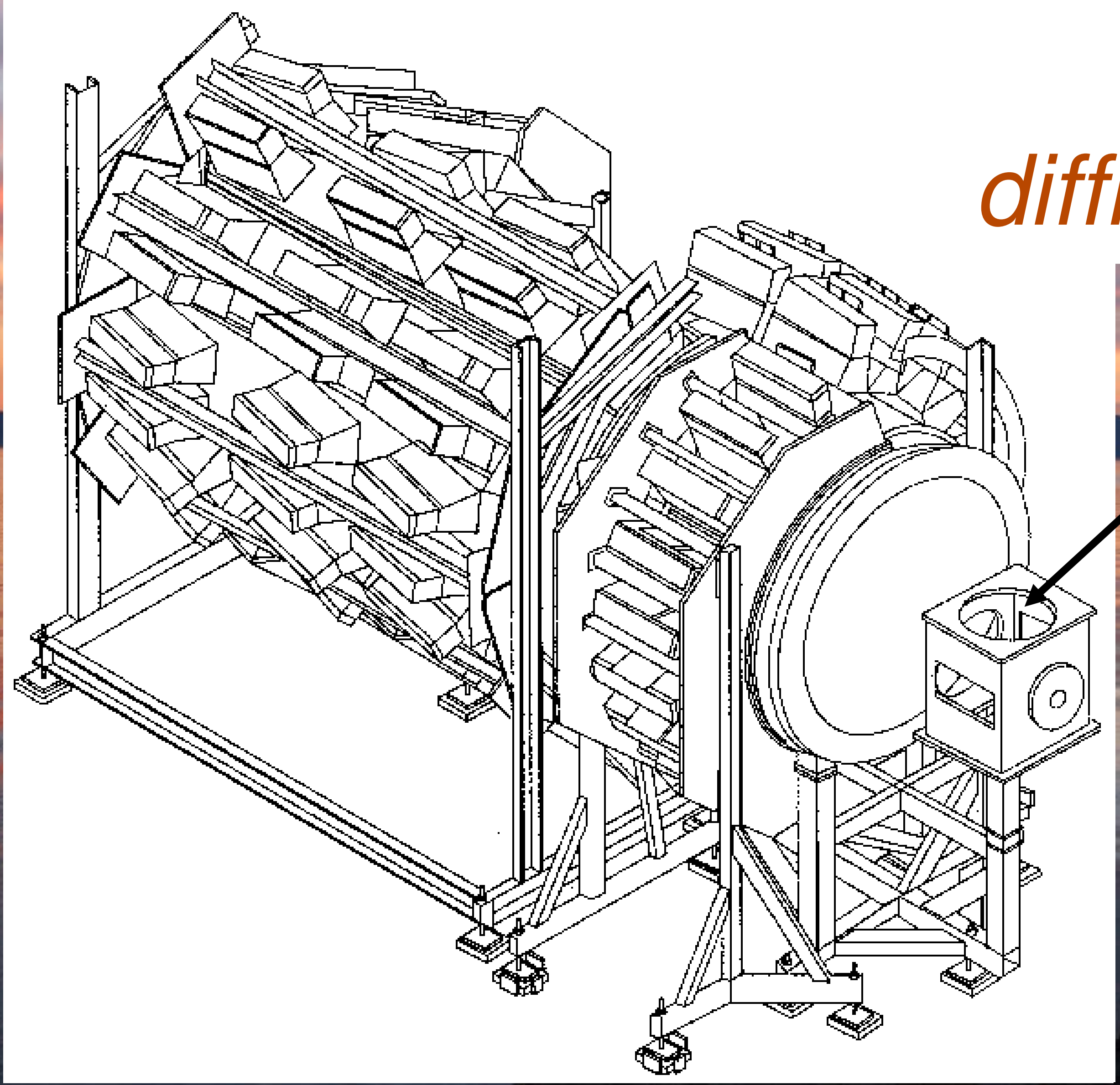
lightsources.org NEWSFLASH

SLAC Researchers Reveal the Dance of Water

“Recent work ... is shedding new light on water’s molecular idiosyncrasies ...”

“These experiments suggested ... two distinct structures, either very disordered or very tetrahedral, exist no matter the temperature.”

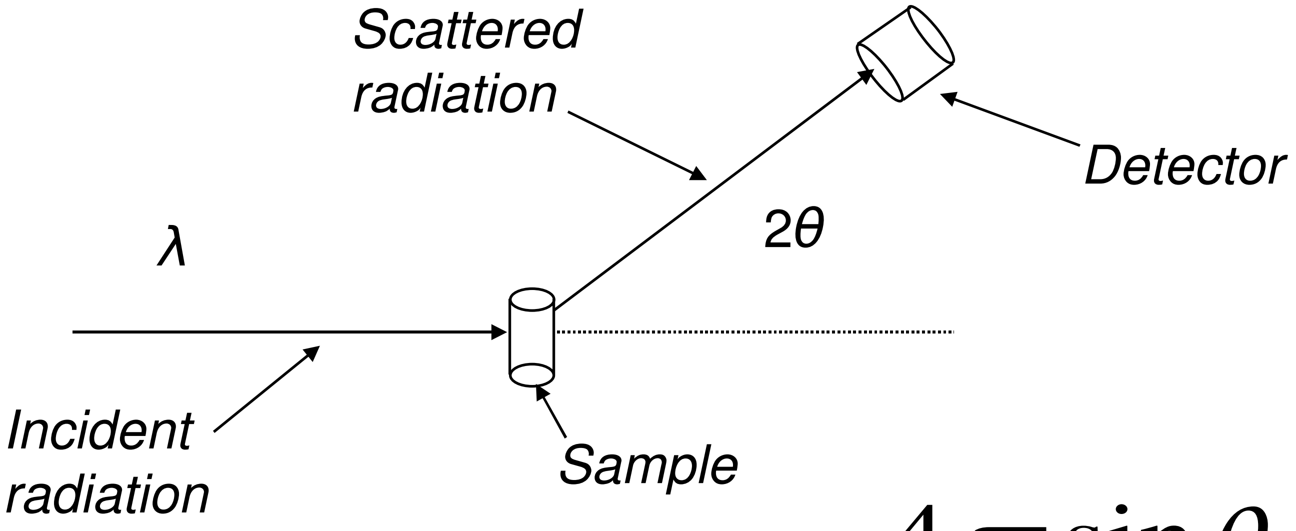
ISIS SANDALS (liquids diffractometer)



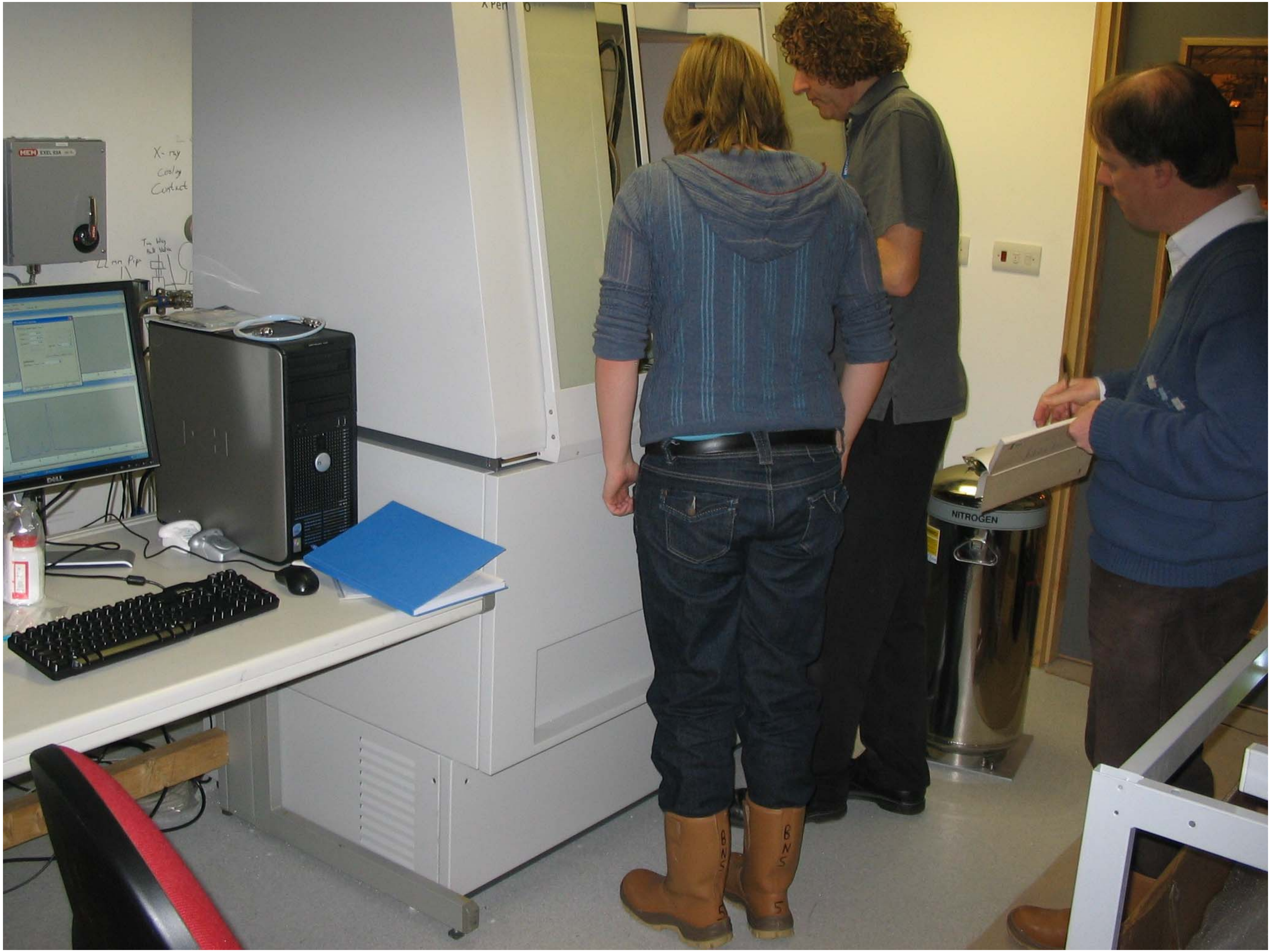
Sample position

Incident neutron beam

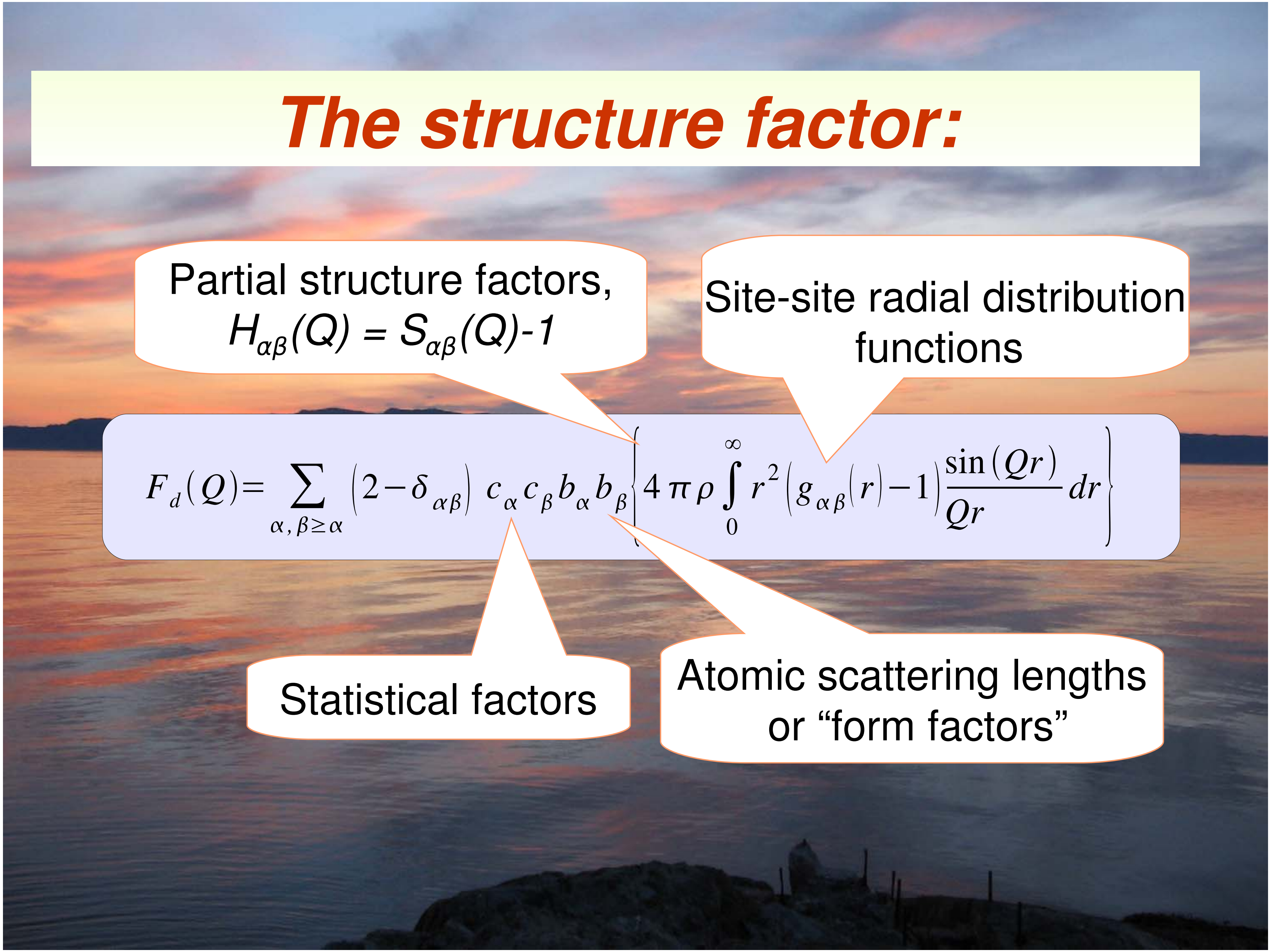
Diffraction from disordered materials - a simple experiment in principle:



$$Q = \frac{4\pi \sin\theta}{\lambda}$$


X-ray
Cooling
Contact
NITROGEN
BNS
BNS

The structure factor:



Partial structure factors,
$H_{\alpha\beta}(Q) = S_{\alpha\beta}(Q)-1$

Site-site radial distribution functions

$$F_d(Q)=\sum_{\alpha,\beta\geq\alpha}\left(2-\delta_{\alpha\beta}\right)\,c_\alpha c_\beta b_\alpha b_\beta\left\{4\pi\rho\int_0^\infty r^2\left(g_{\alpha\beta}(r)-1\right)\frac{\sin(Qr)}{Qr}\,dr\right\}$$

Statistical factors

Atomic scattering lengths
or “form factors”

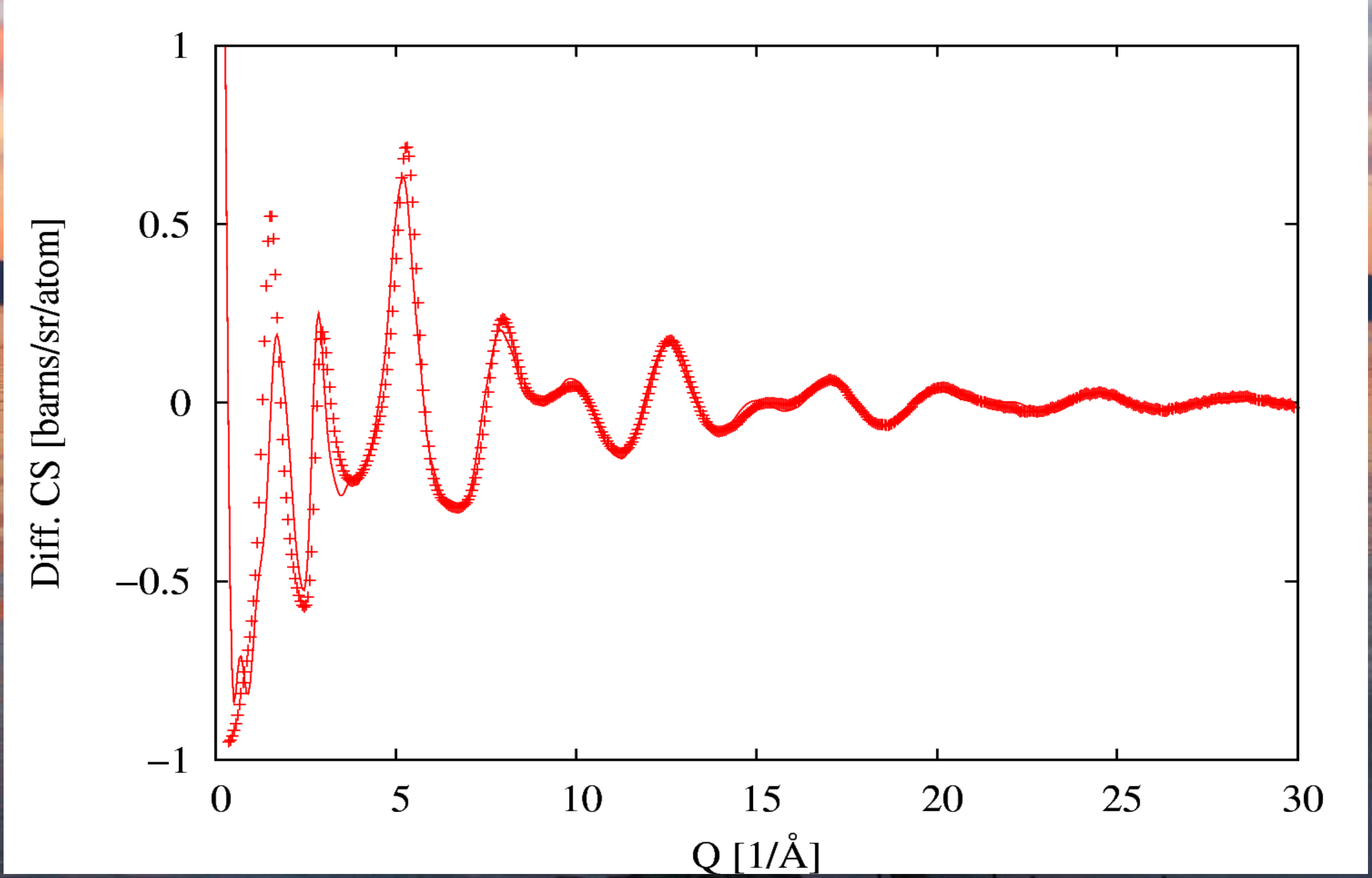
Empirical potential structure refinement (EPSR):-

- Use harmonic constraints to define molecules.
  - Molecules are rigid but disordered to simulate zero point energy effects.
- Set up a “reference” potential energy function for site-site interactions.
- Use the diffraction data to perturb this reference potential energy function.
- Accept or reject moves on the basis of

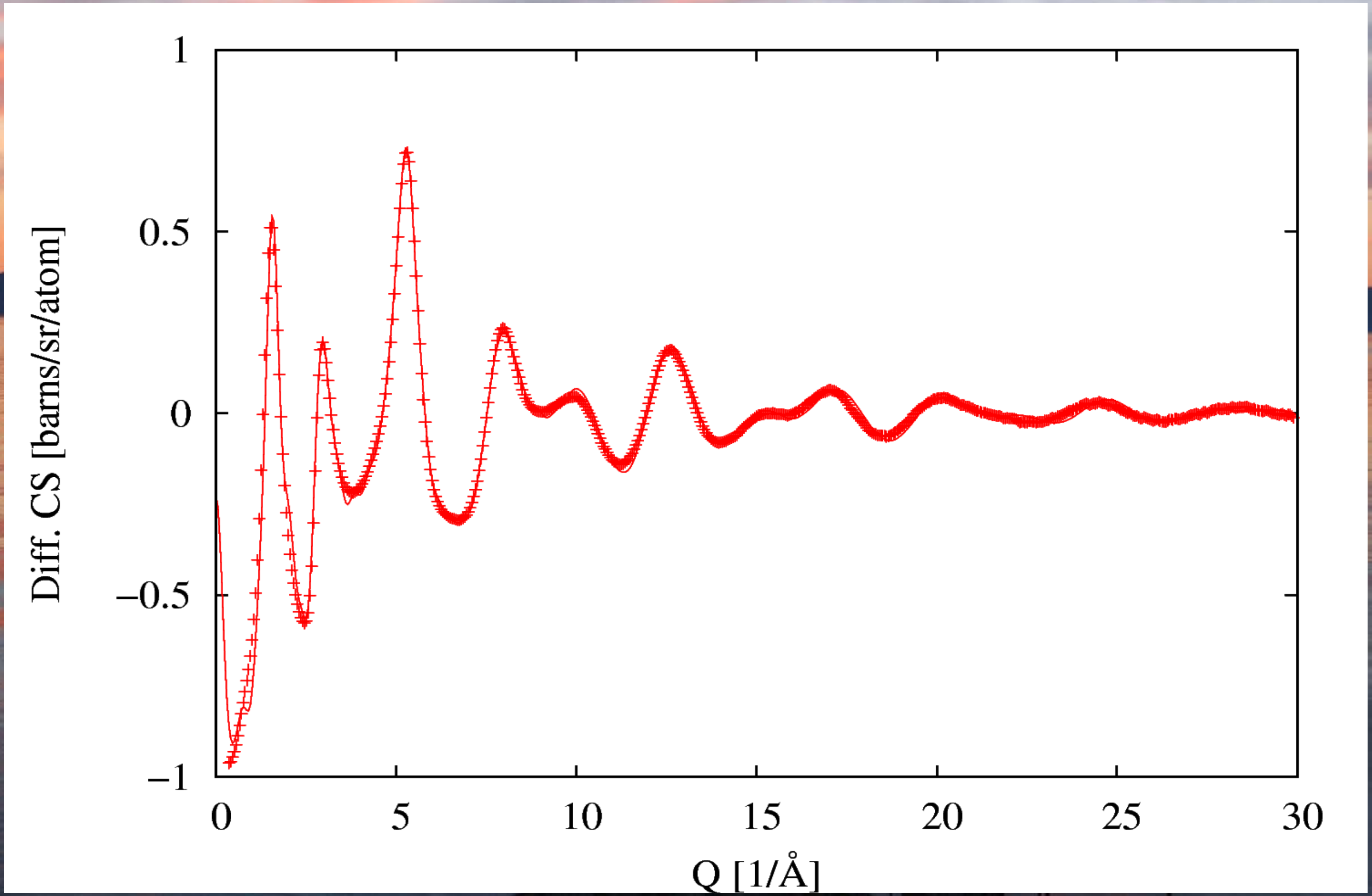
$$\Delta U = \Delta U_{ref} + \Delta U_{ep}$$

- See *Phys. Rev. B.*, **72**, 104204, (2005)

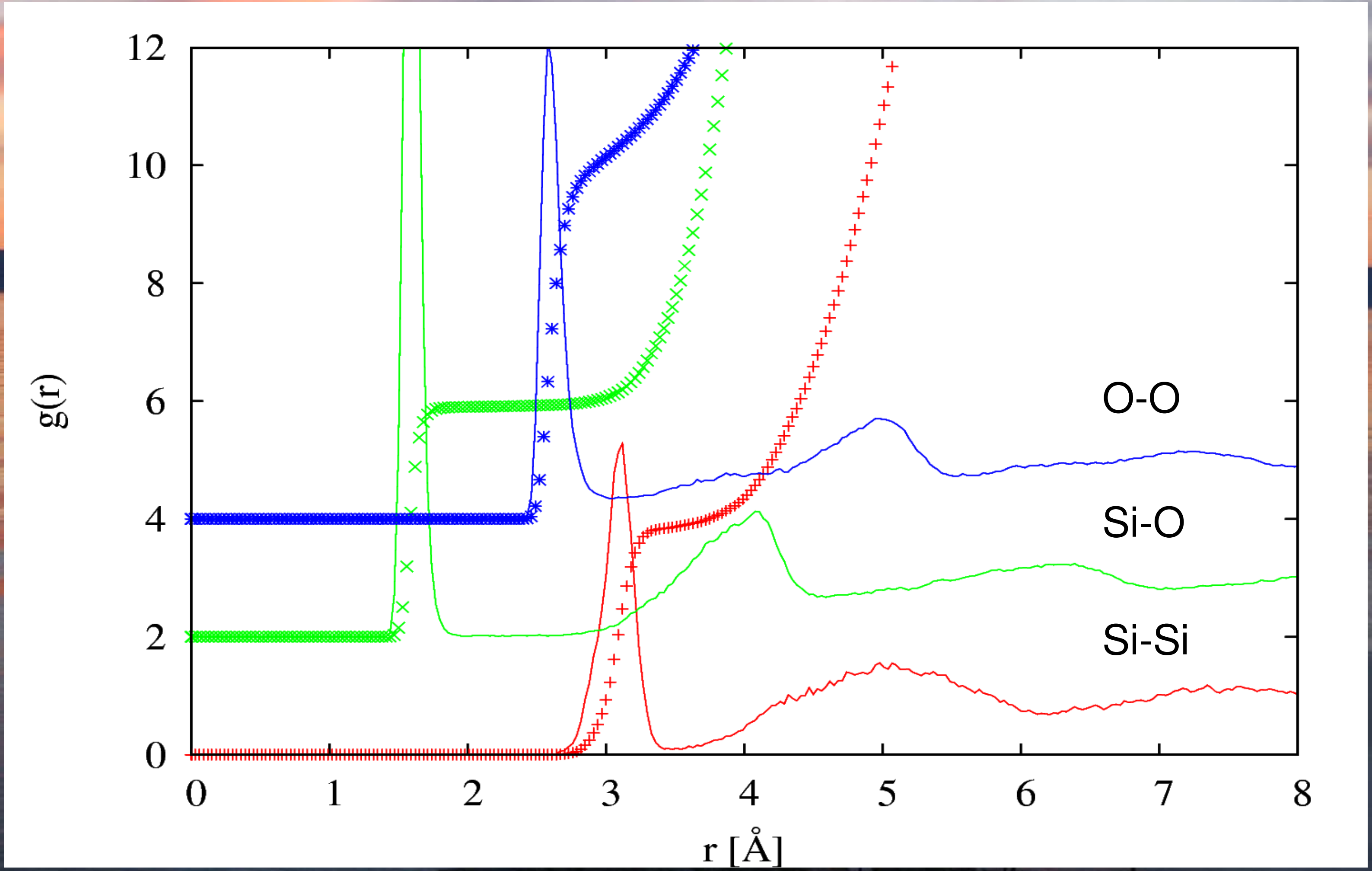
Application of the reference potential – amorphous silica



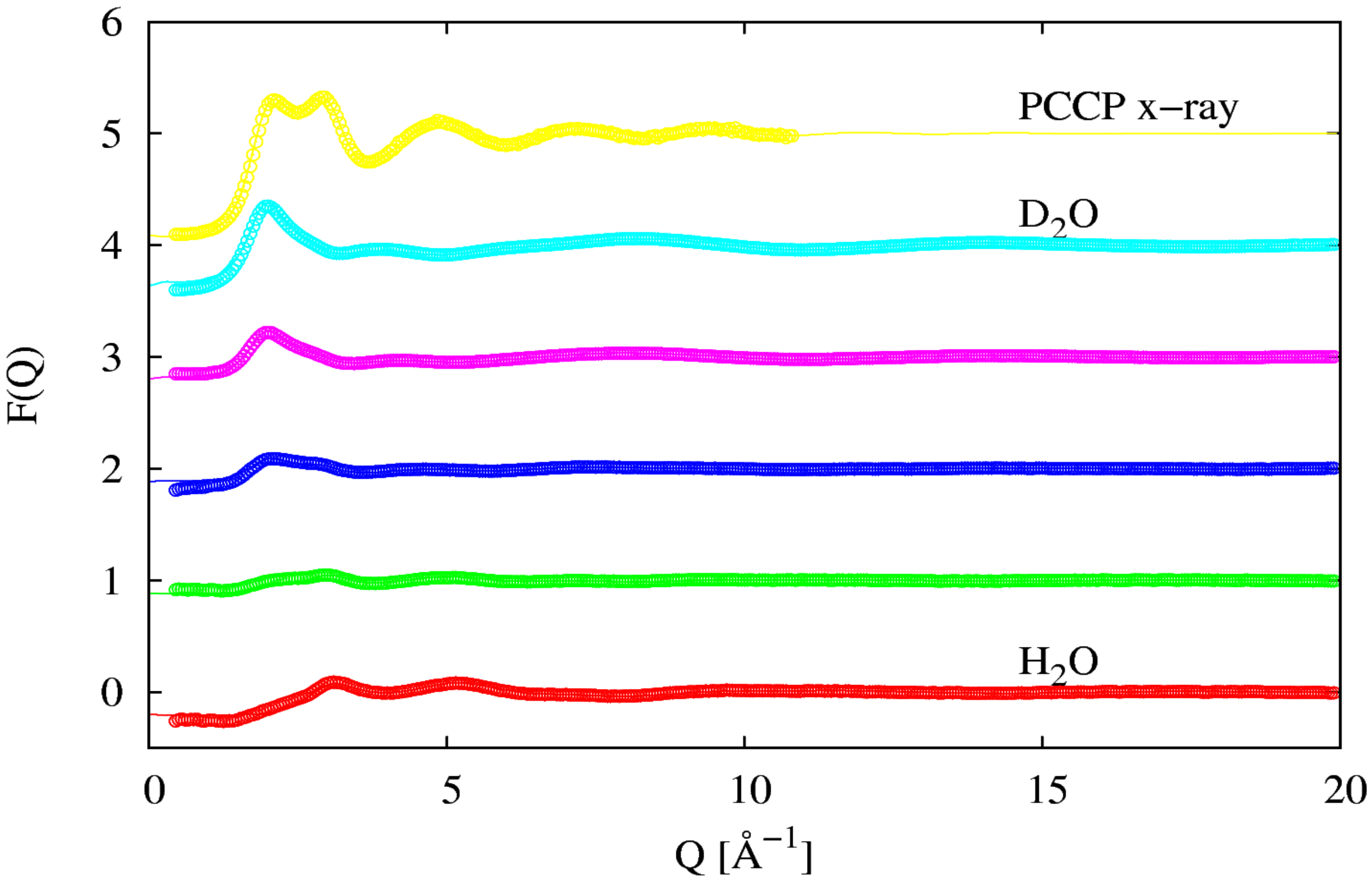
Refinement with the empirical potential – amorphous silica



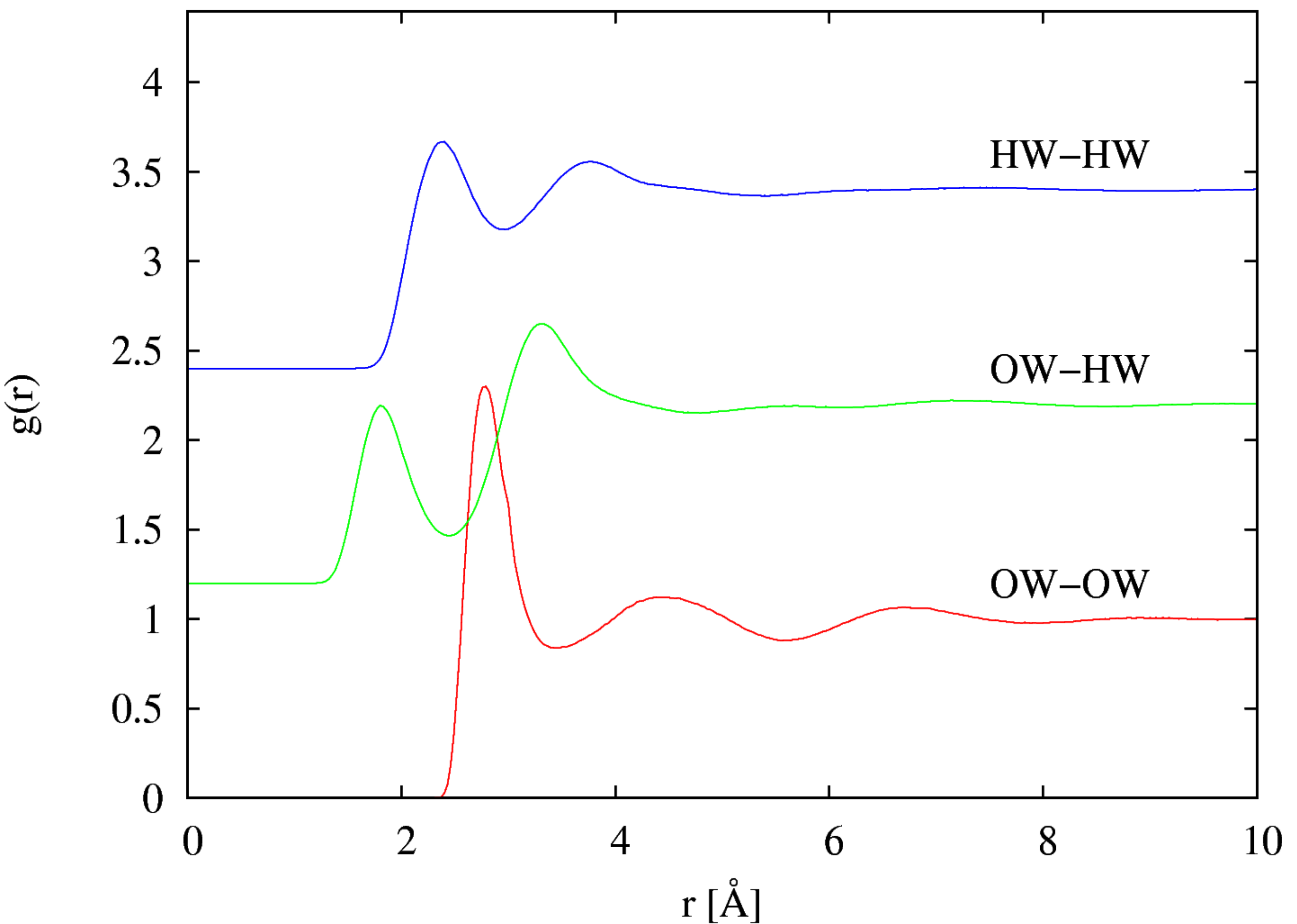
Refinement with the empirical potential – amorphous silica



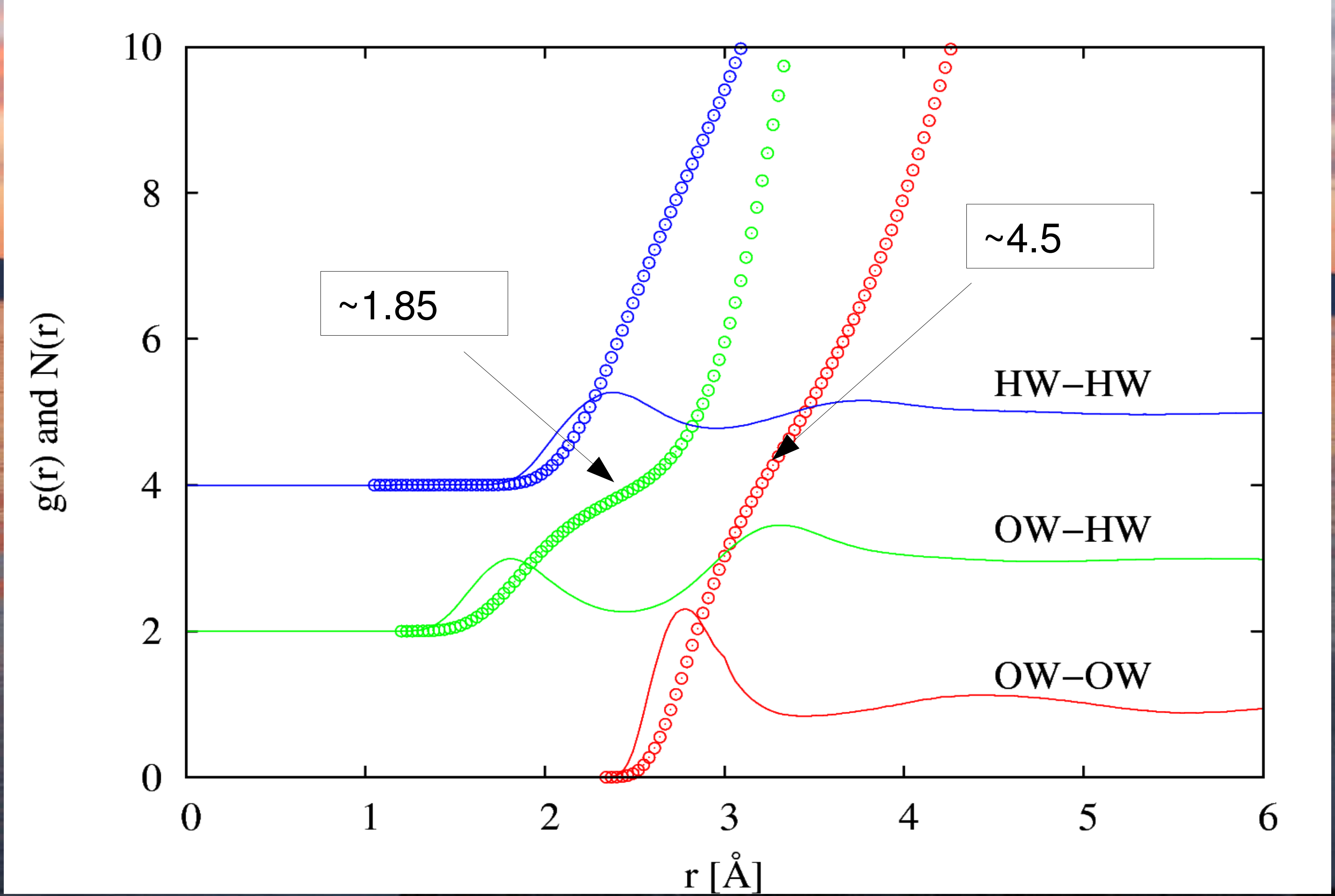
Refinement with the empirical potential – water



Water g(r)s:



Water coordination numbers:



Evidence for heterogeneities?

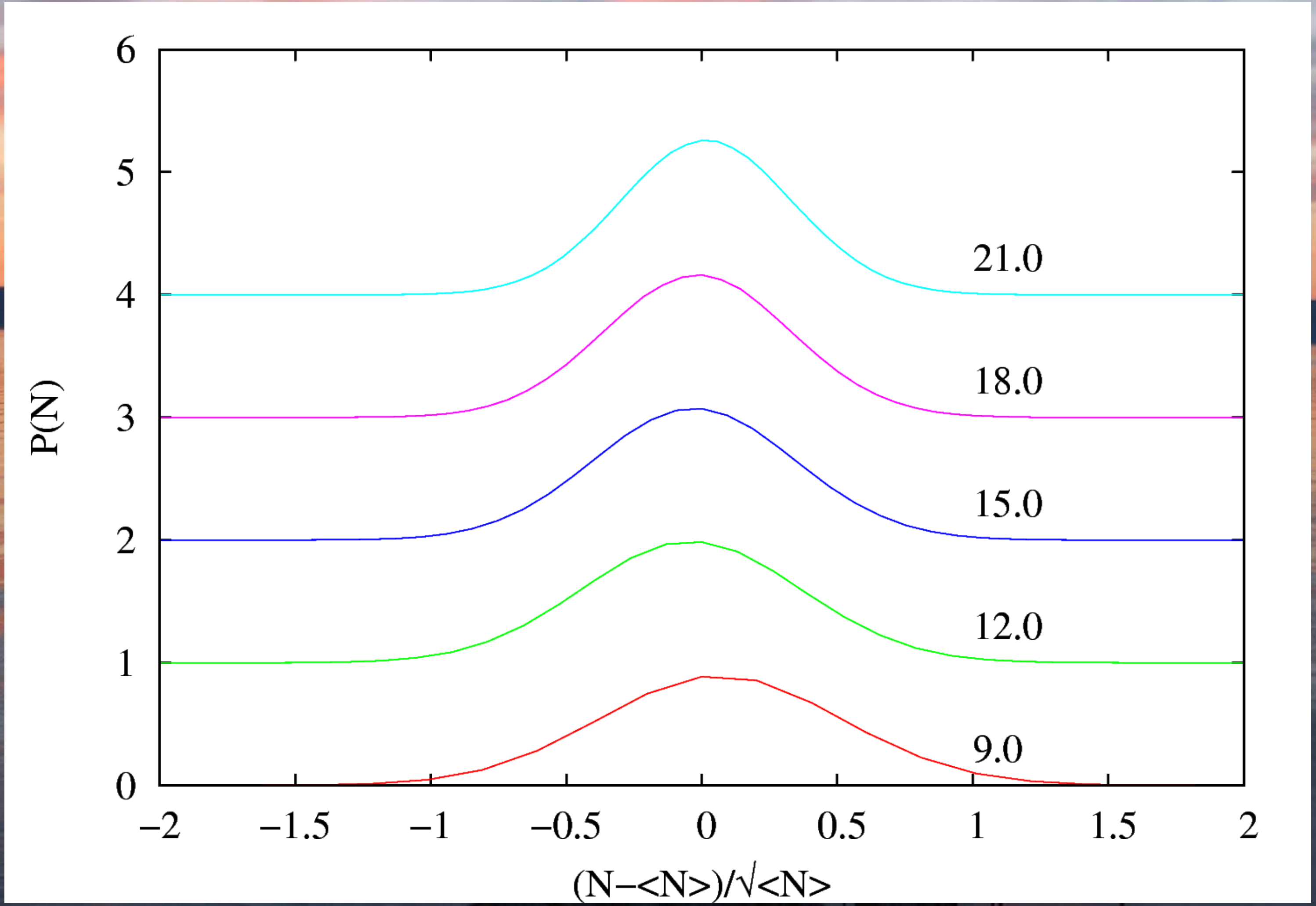
Calculate number fluctuations:

$$S(0)=\frac{\langle (N-\langle N\rangle)^2\rangle}{\langle N\rangle}$$

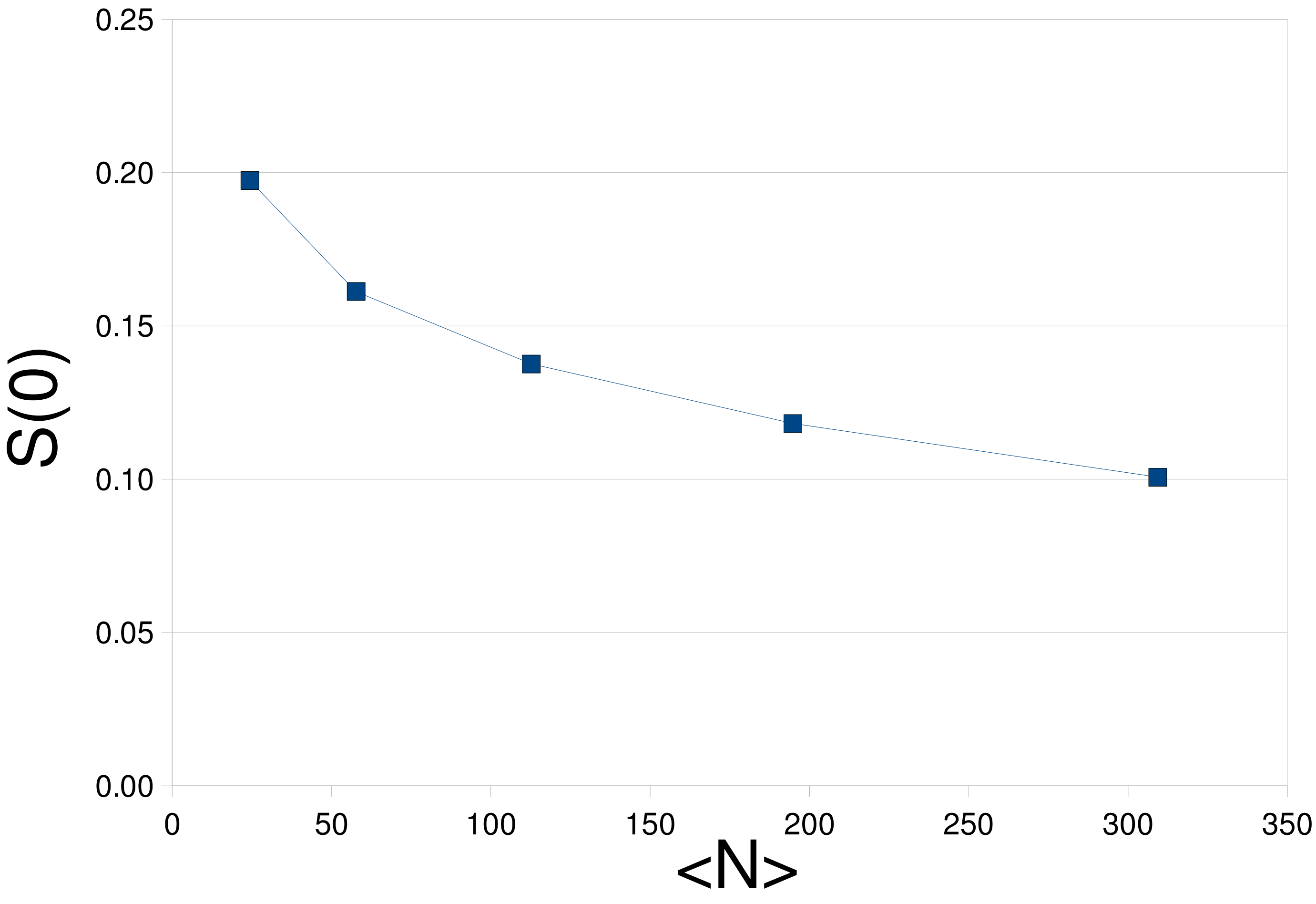
- Choose sample box sizes < simulation box size
- Form ensemble average of *S*(0)
- Calculate probability distribution v. $\frac{\langle (N-\langle N\rangle)\rangle}{\sqrt{\langle N\rangle}}$

  (Hummer et. al., PNAS, 1996)

Distribution of fluctuations in EPSR water



Fluctuations in EPSR water



Inconclusive – so far – try Lennard-Jonesium

- Lennard-Jonesium has a critical point:

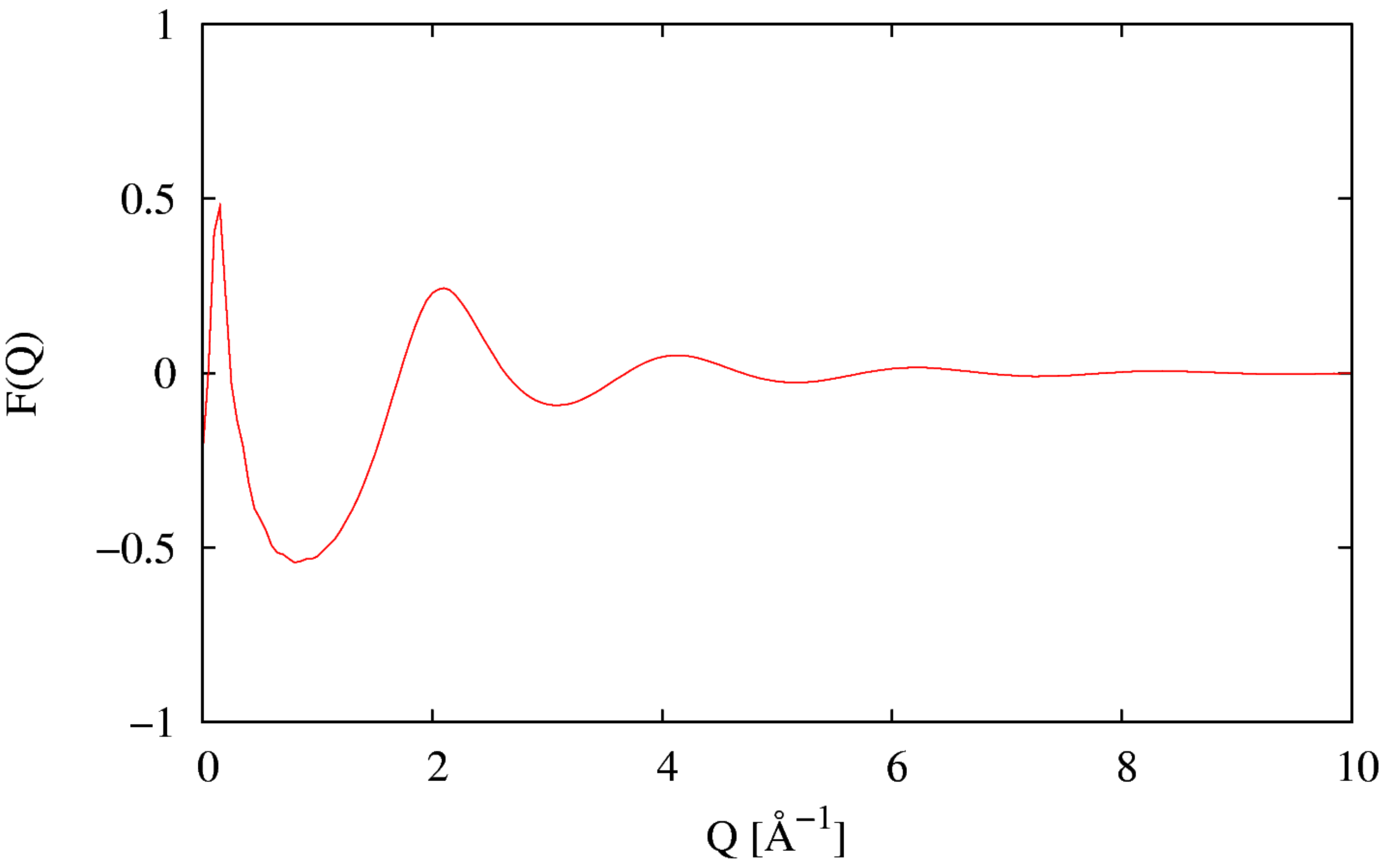
$$T_c = \text{۱.۱۸۷۶}\,\epsilon$$

$$\rho_c = \frac{\text{۰.۳۱۹۷}}{\sigma^{\text{۳}}}$$

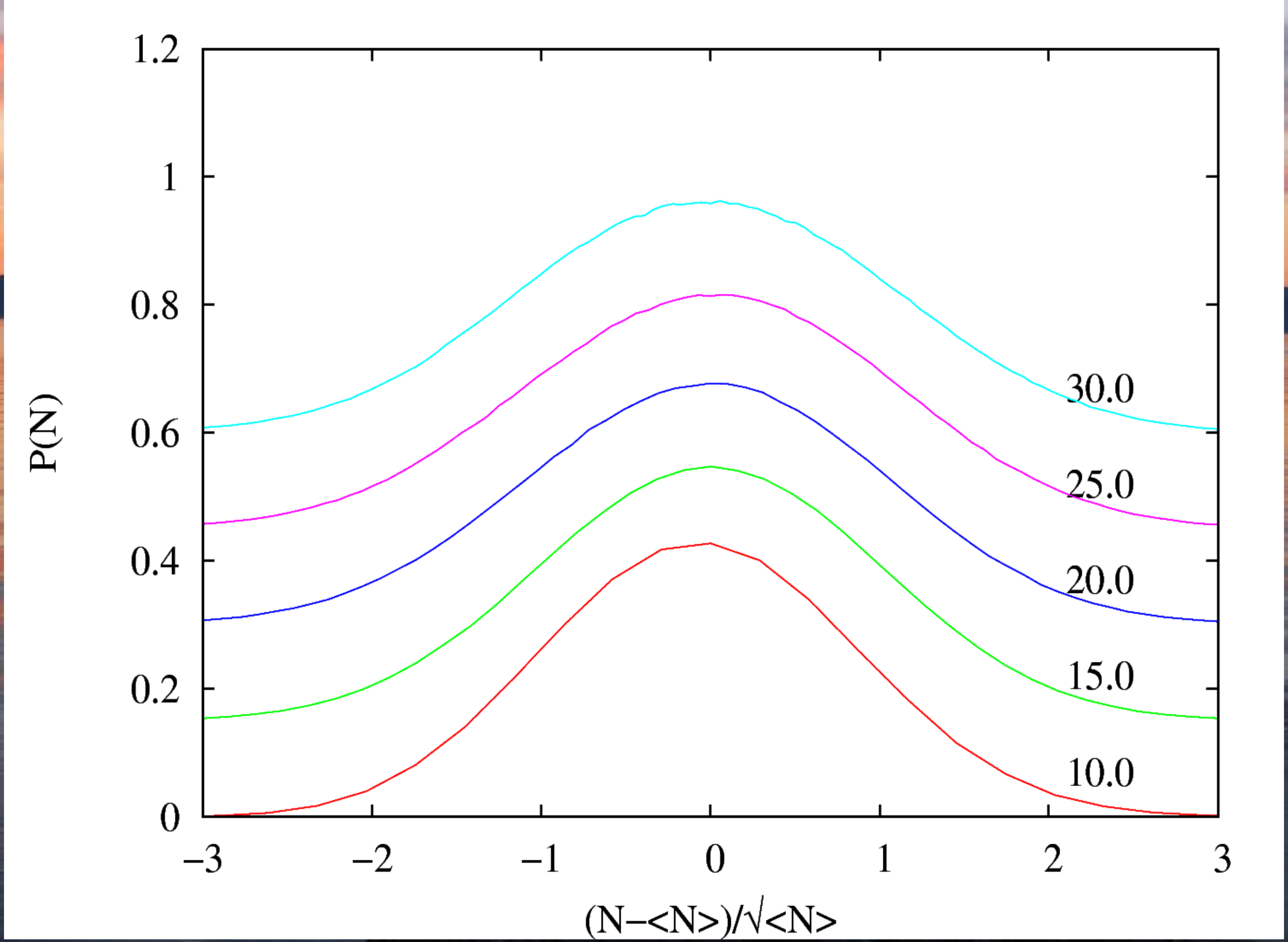
(e.g. N. B. Wilding, PRE, 52, p 602 (1998))

- Calculate S(Q) and density fluctuations for $T \sim T_c$, $\rho = \rho_c$

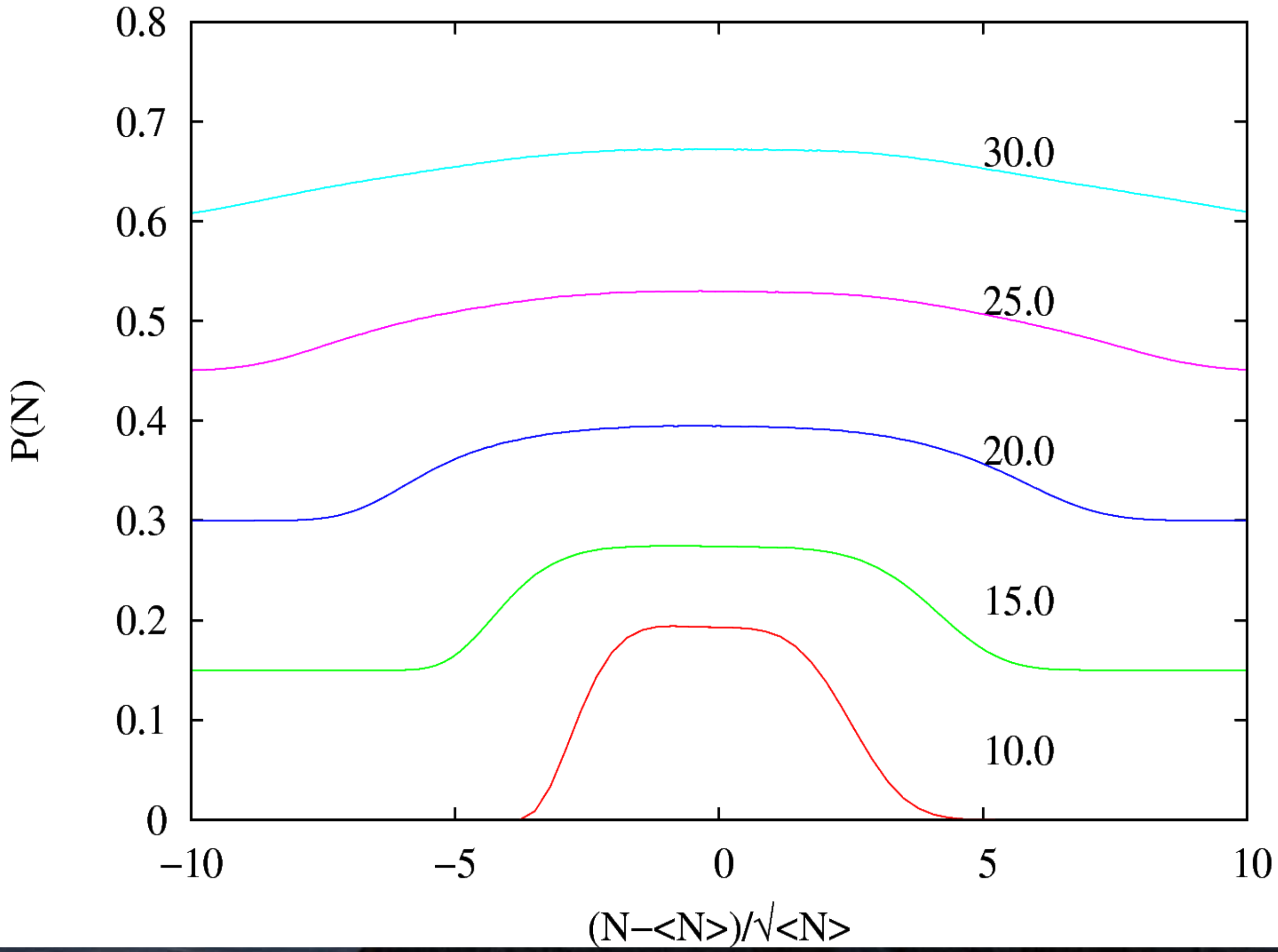
S(Q) at T = 1.37Tc



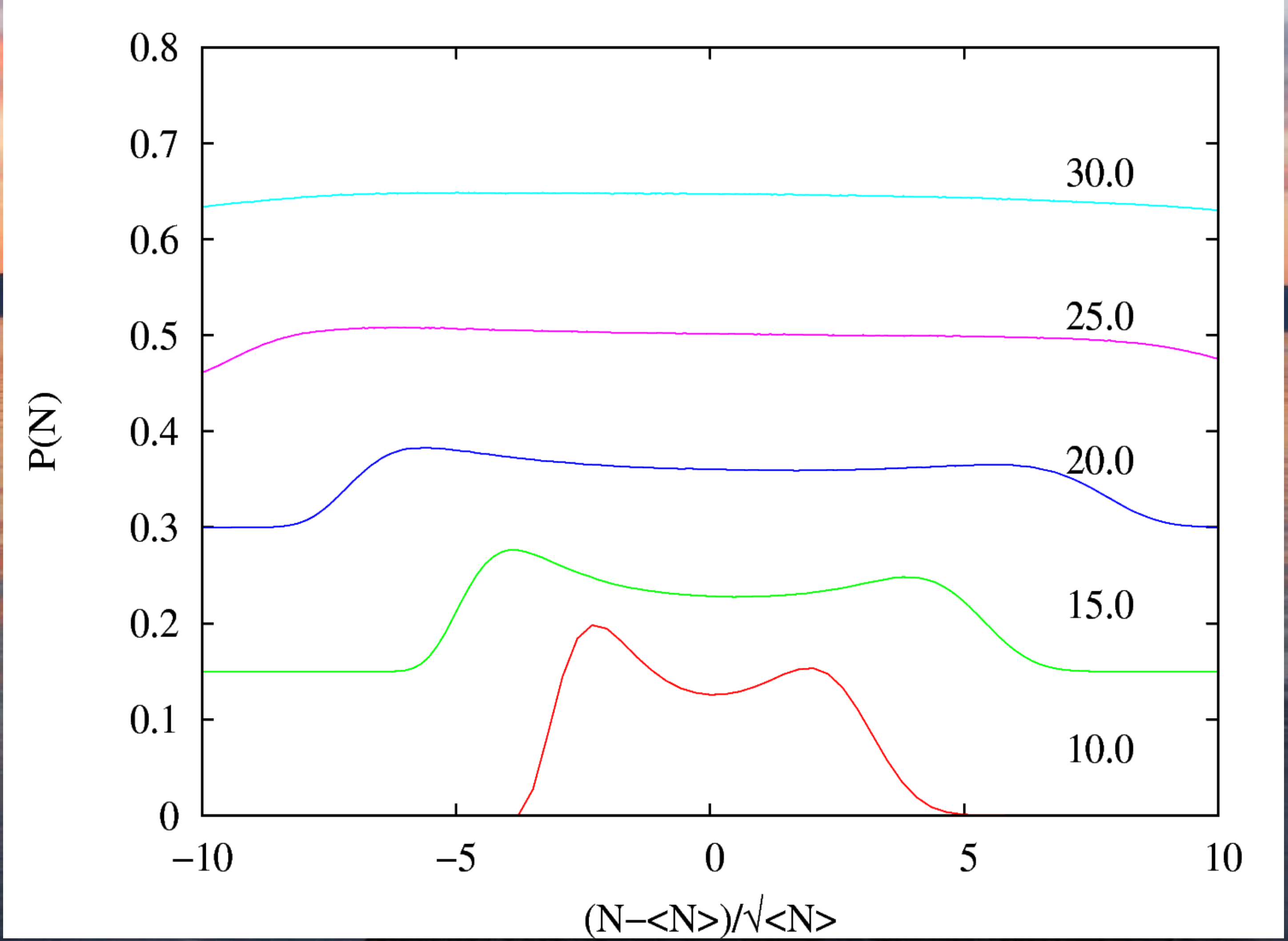
Fluctuations at T = 1.37Tc



Fluctuations at T = 1.02Tc

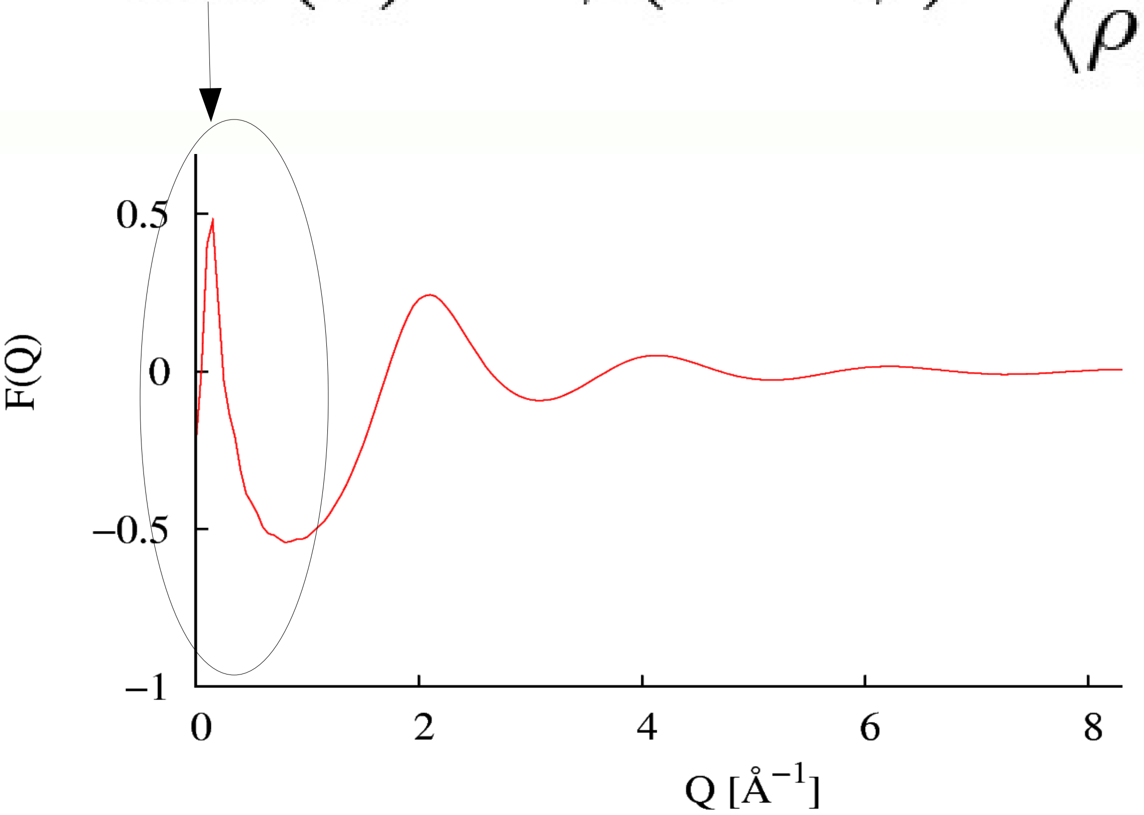


Fluctuations at T = 0.98Tc



Evidence from small angle theory (Glatter and Kratky, 1982)

$$S_A(0) = \phi(1-\phi)\frac{(\Delta\rho)^2}{\langle\rho\rangle}v_c$$



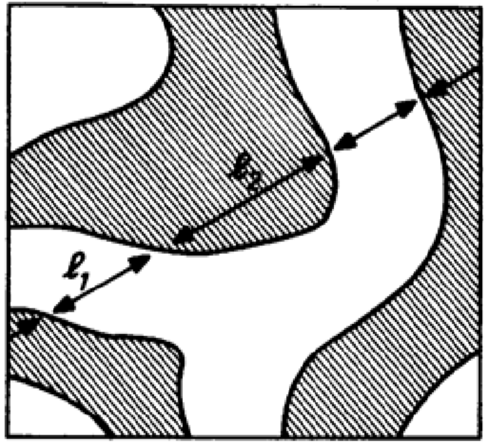
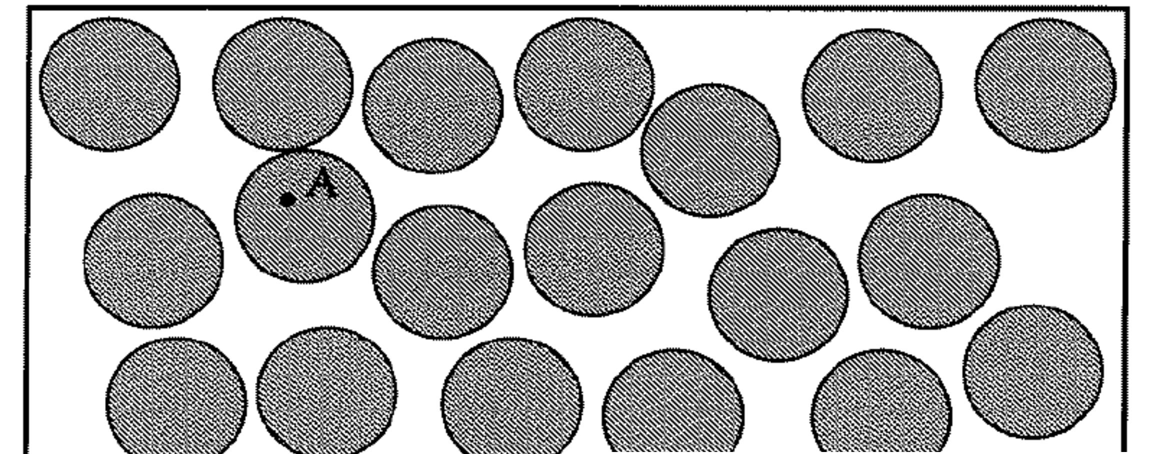


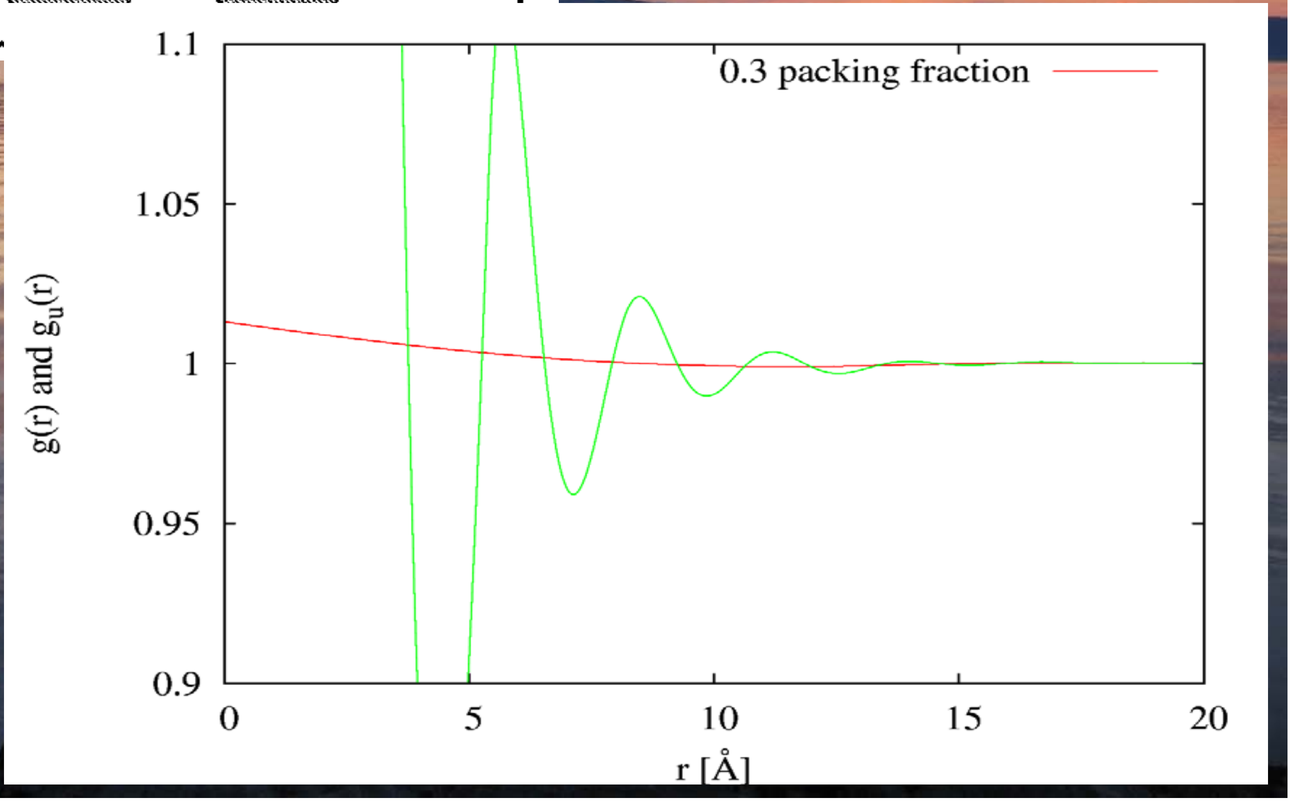
FIG. 6. Non-particulate two-phase system (schematic).

“Colloidal” sphere model

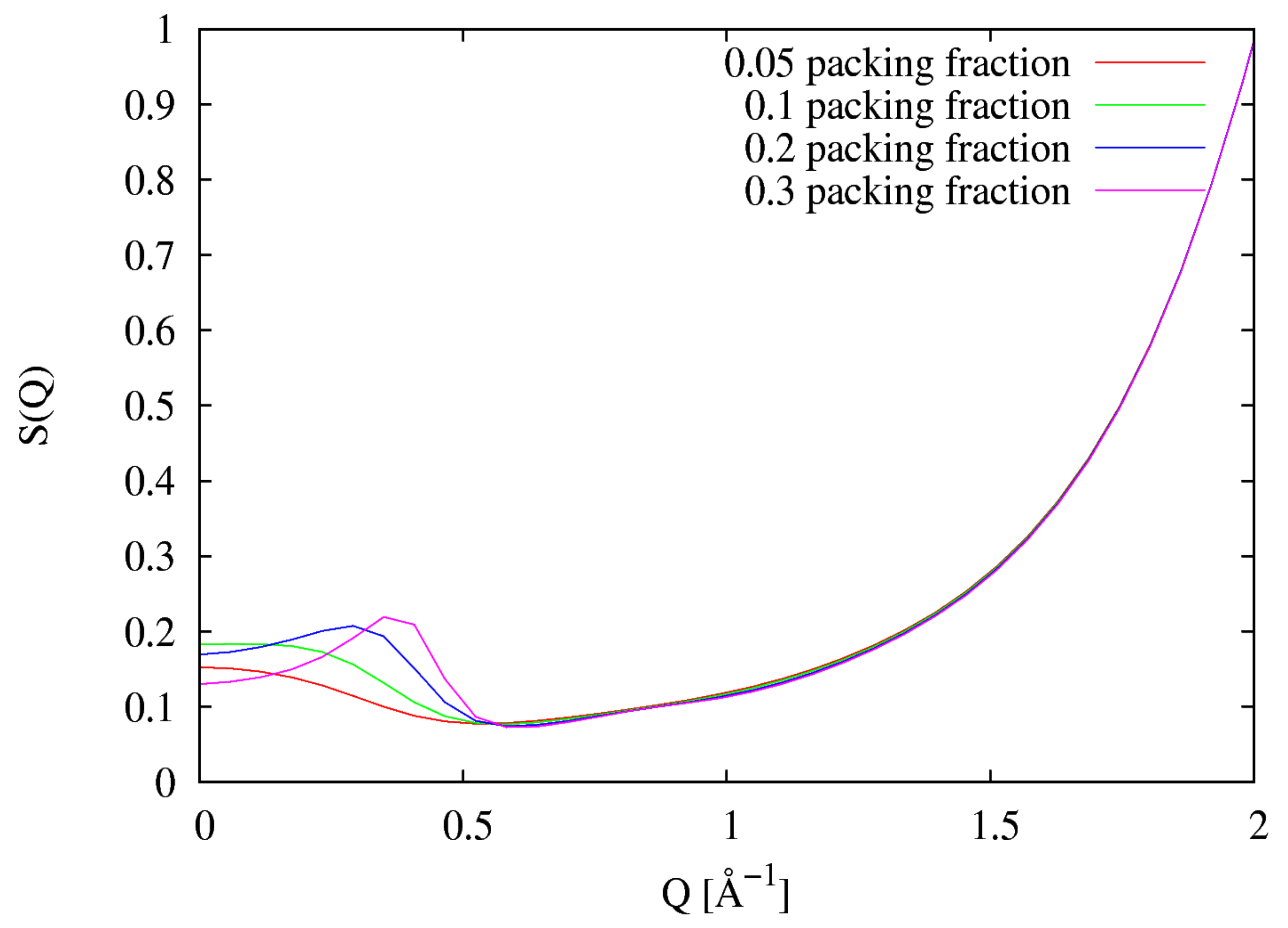


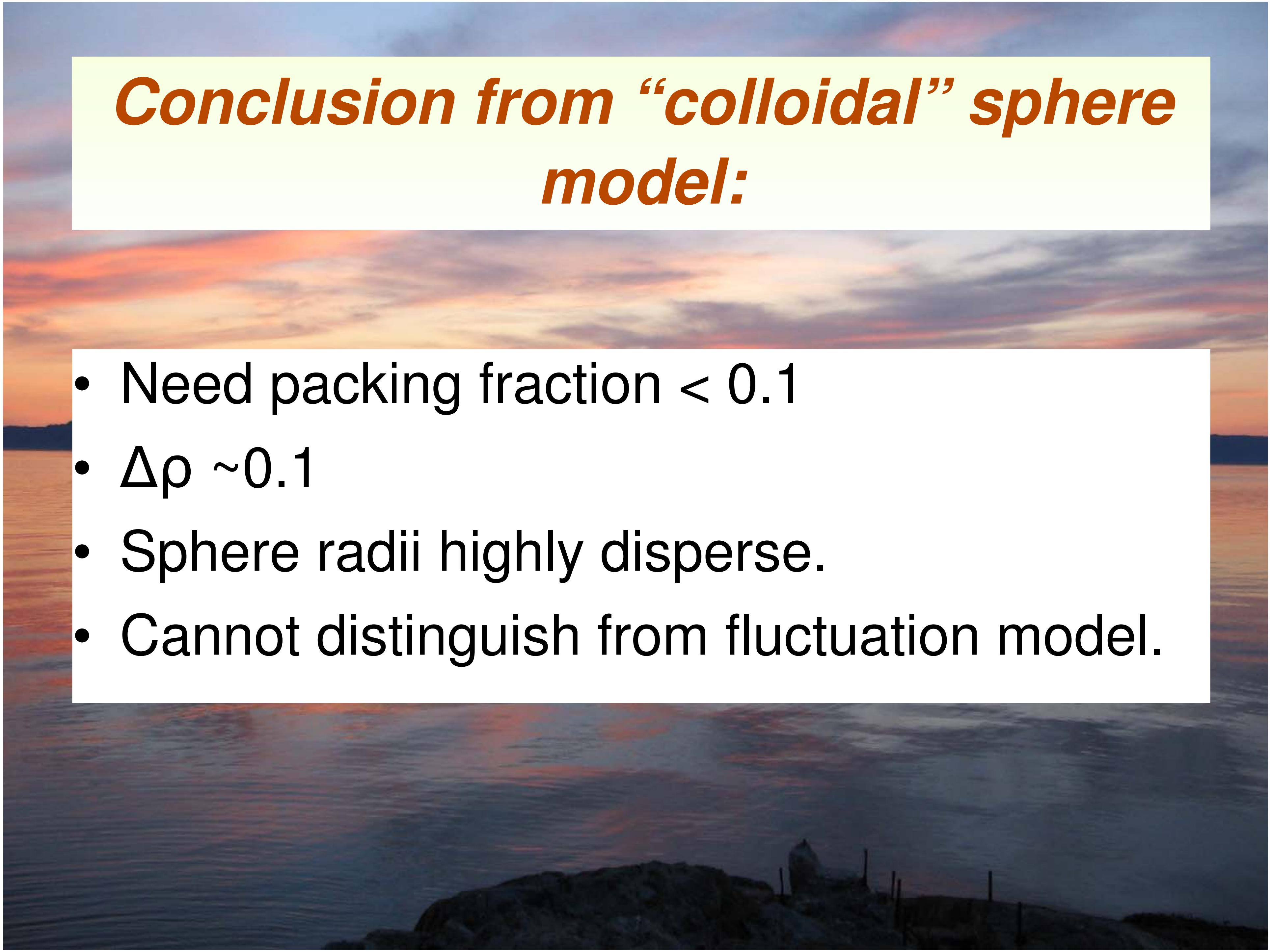
(Soper, JPCM, 1997)

$$g'(r) = g(r) * g_u(r)$$



“Colloidal” sphere model

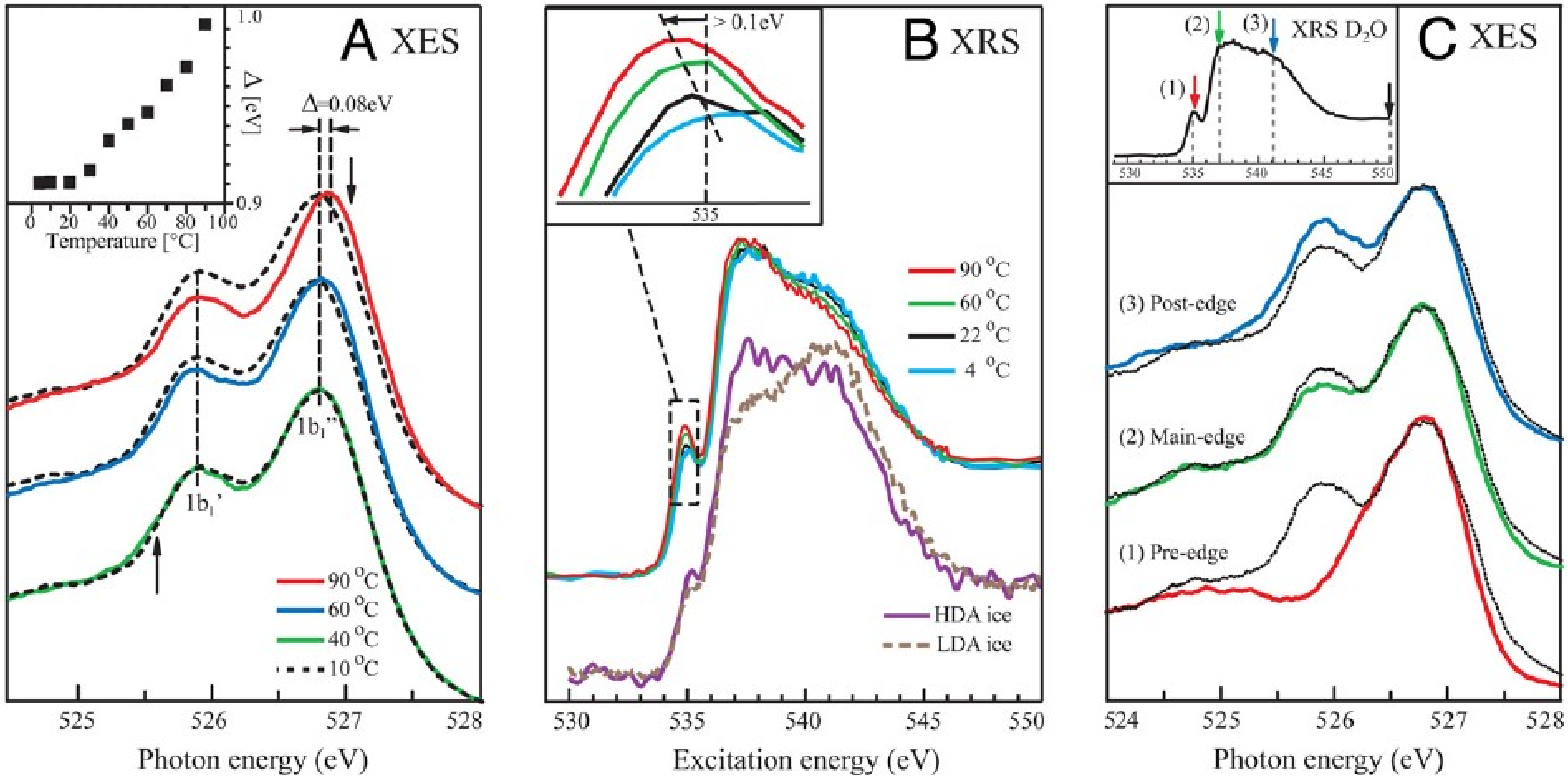




Conclusion from "colloidal" sphere model:

- Need packing fraction < 0.1
- $\Delta\rho \sim 0.1$
- Sphere radii highly disperse.
- Cannot distinguish from fluctuation model.

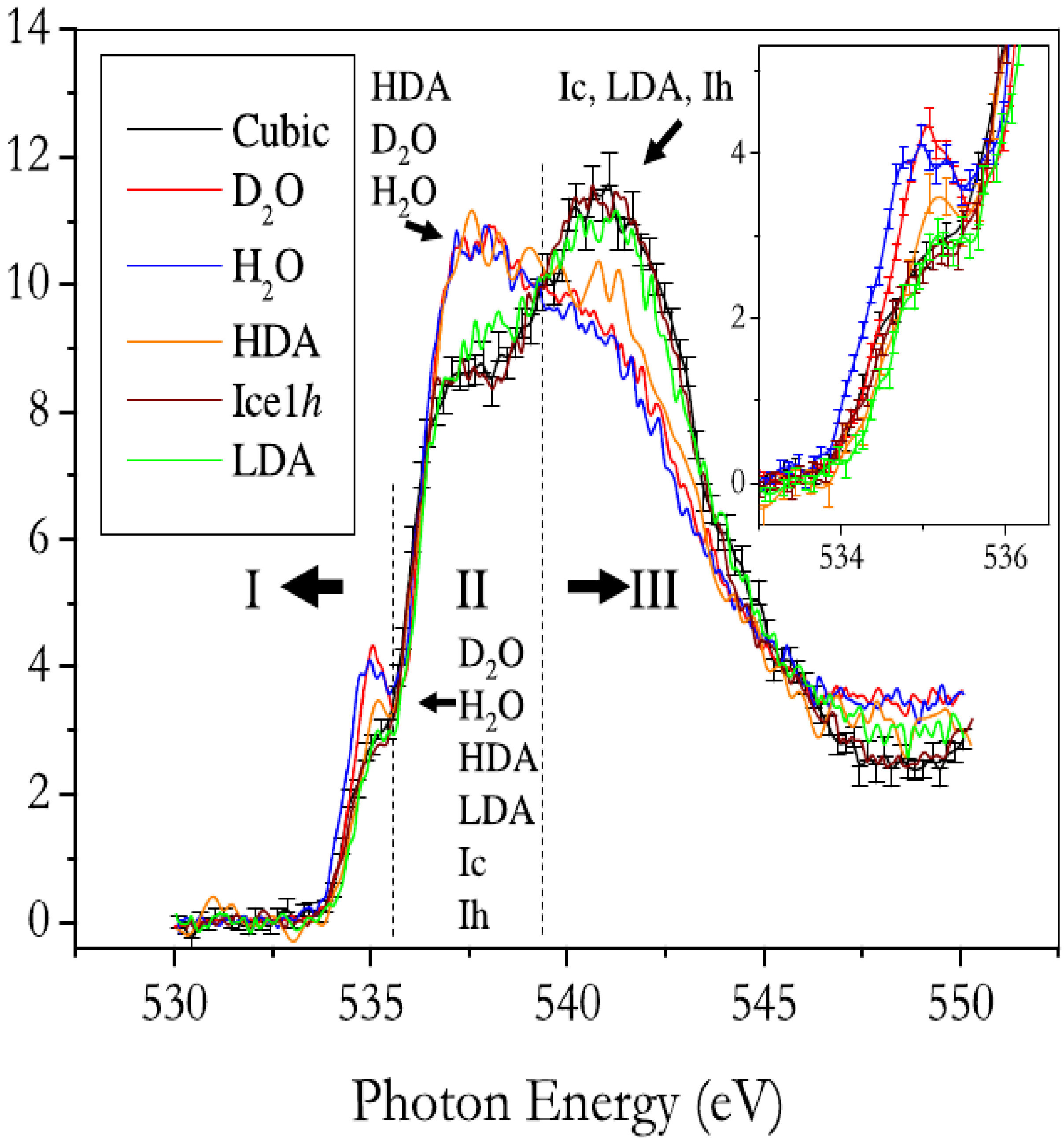
Evidence from XAS/XES?



Evidence from XAS/XES?

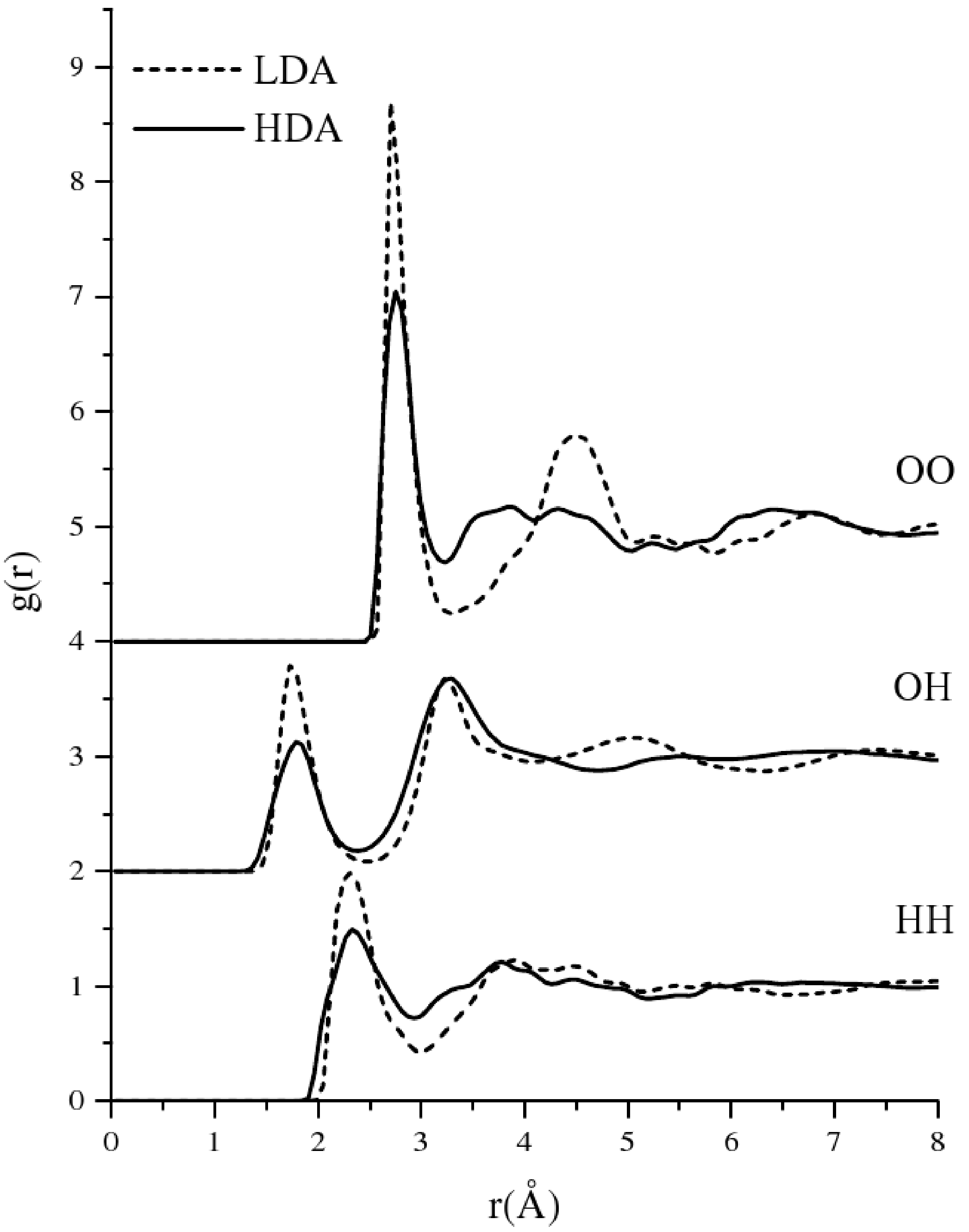
Amorphous ice

Tse, et. al. PRL 2008

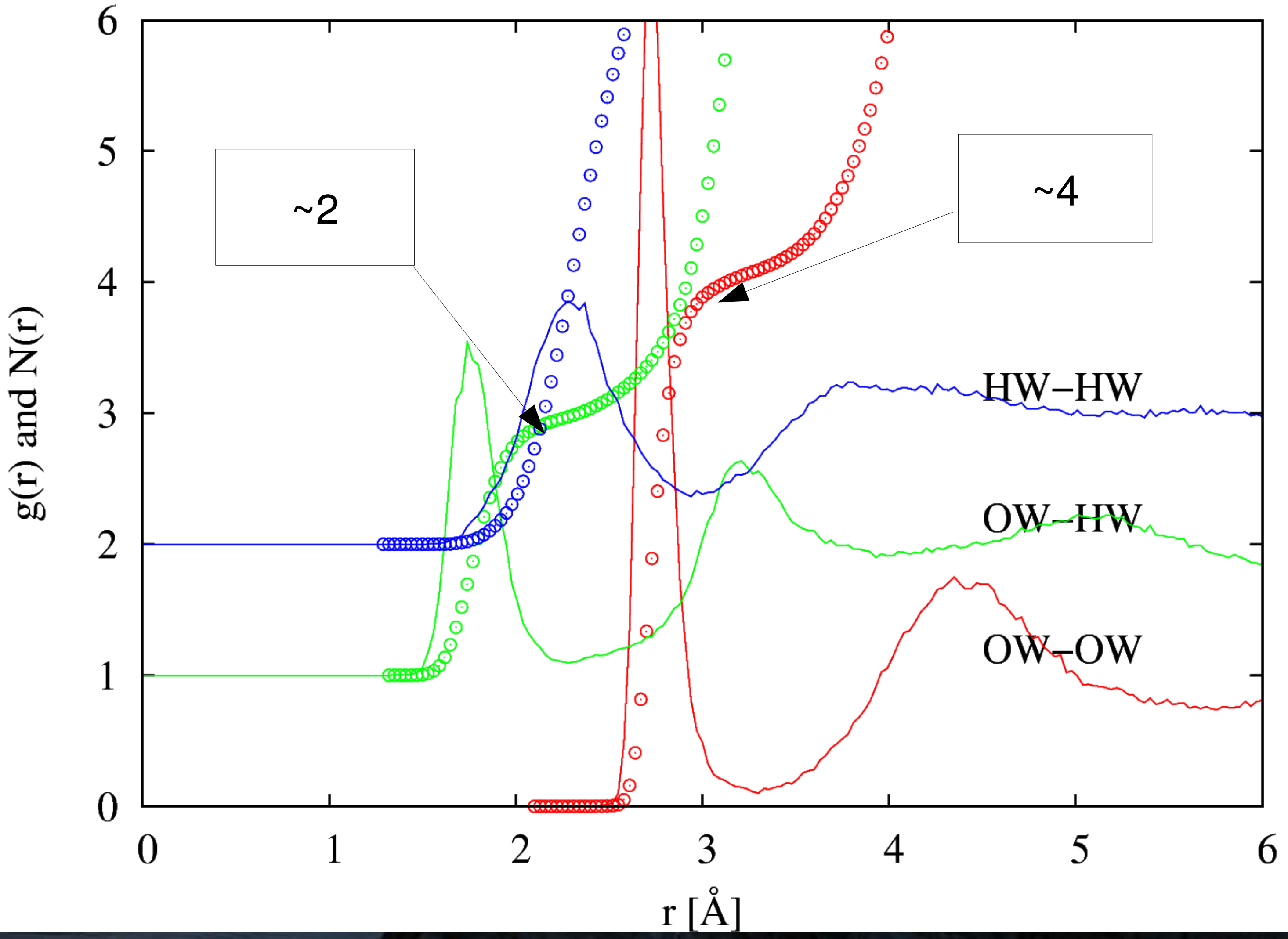


Evidence from XAS/XES? Amorphous ice

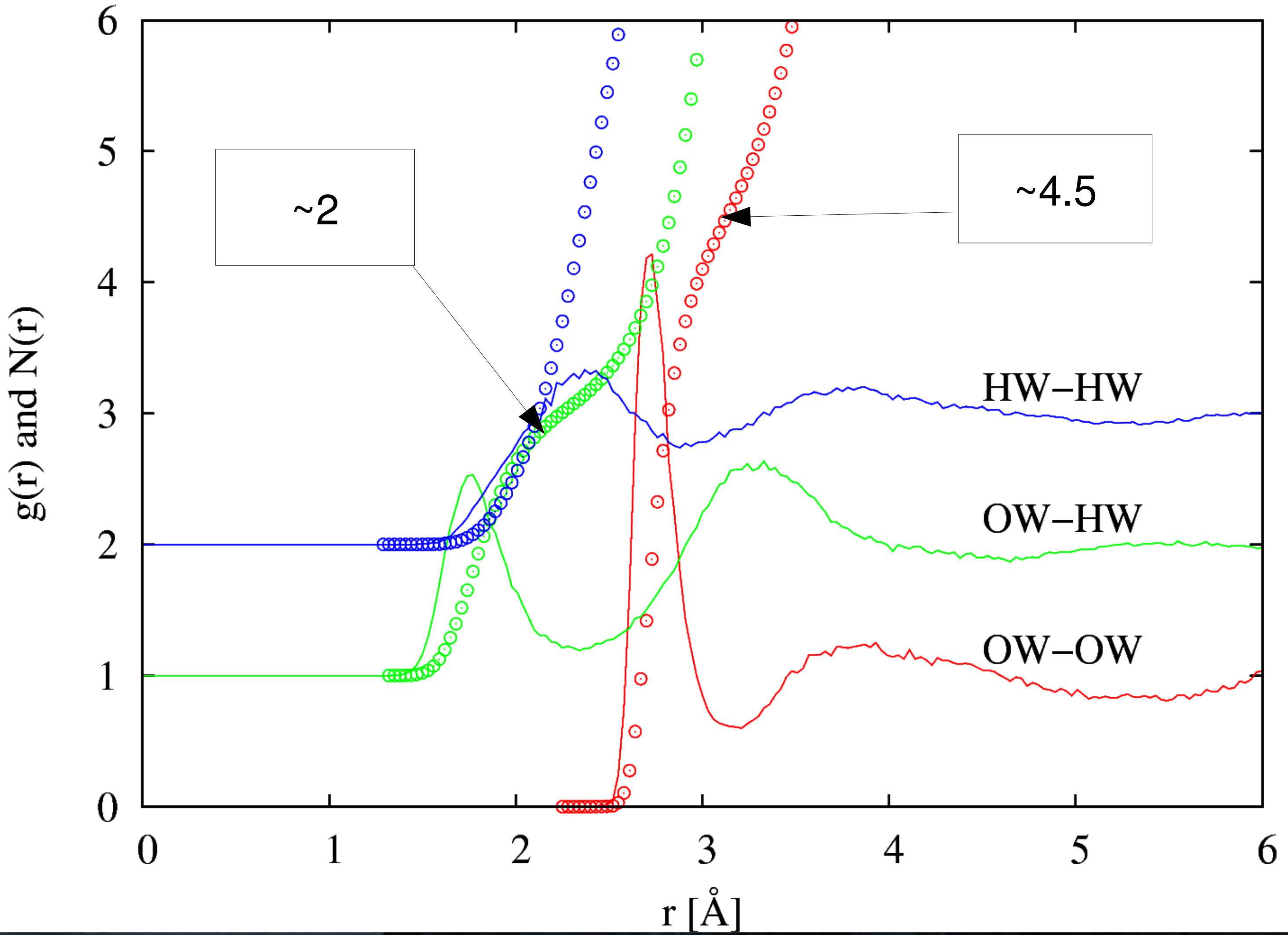
Finney et. al. PRL, 2002



Low density amorphous ice



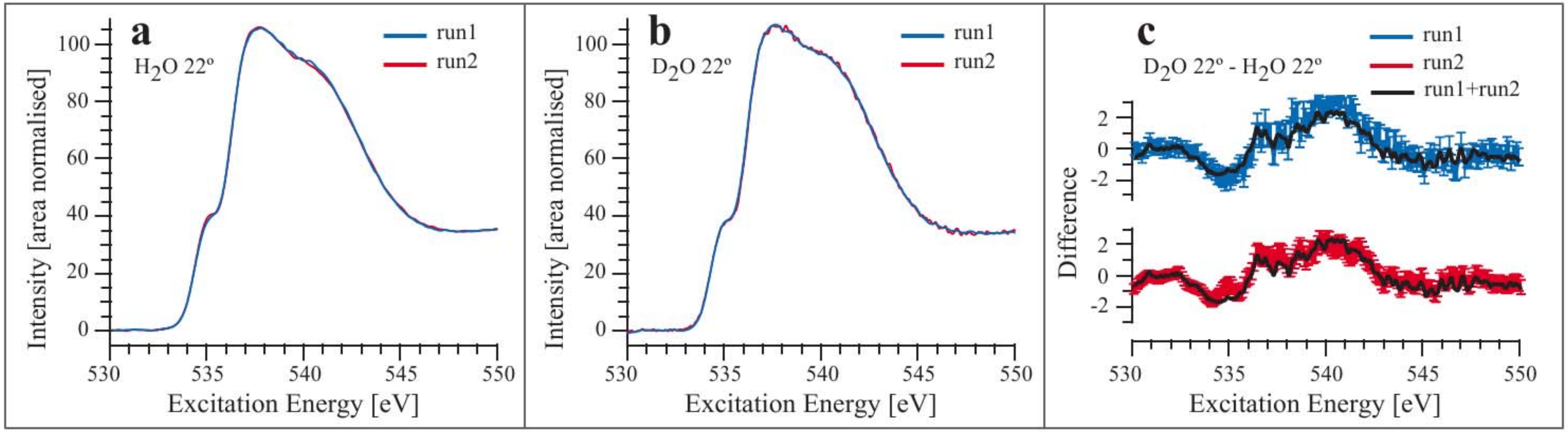
High density amorphous ice



~2

~4.5

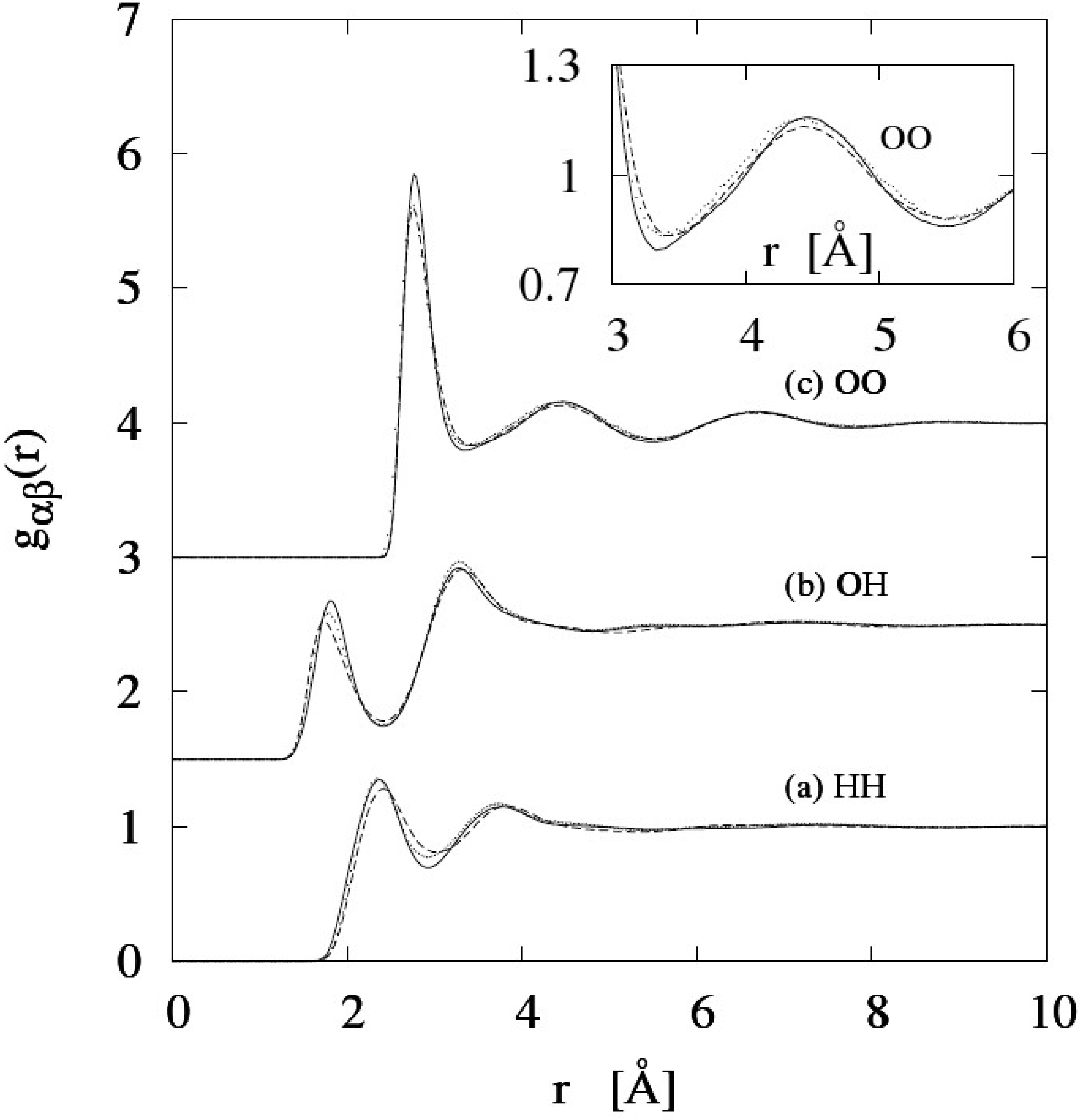
Evidence from XAS/XES?
H20/D20
Bergmann et. al. Phys. Rev B 2007



Evidence from XAS/XES?

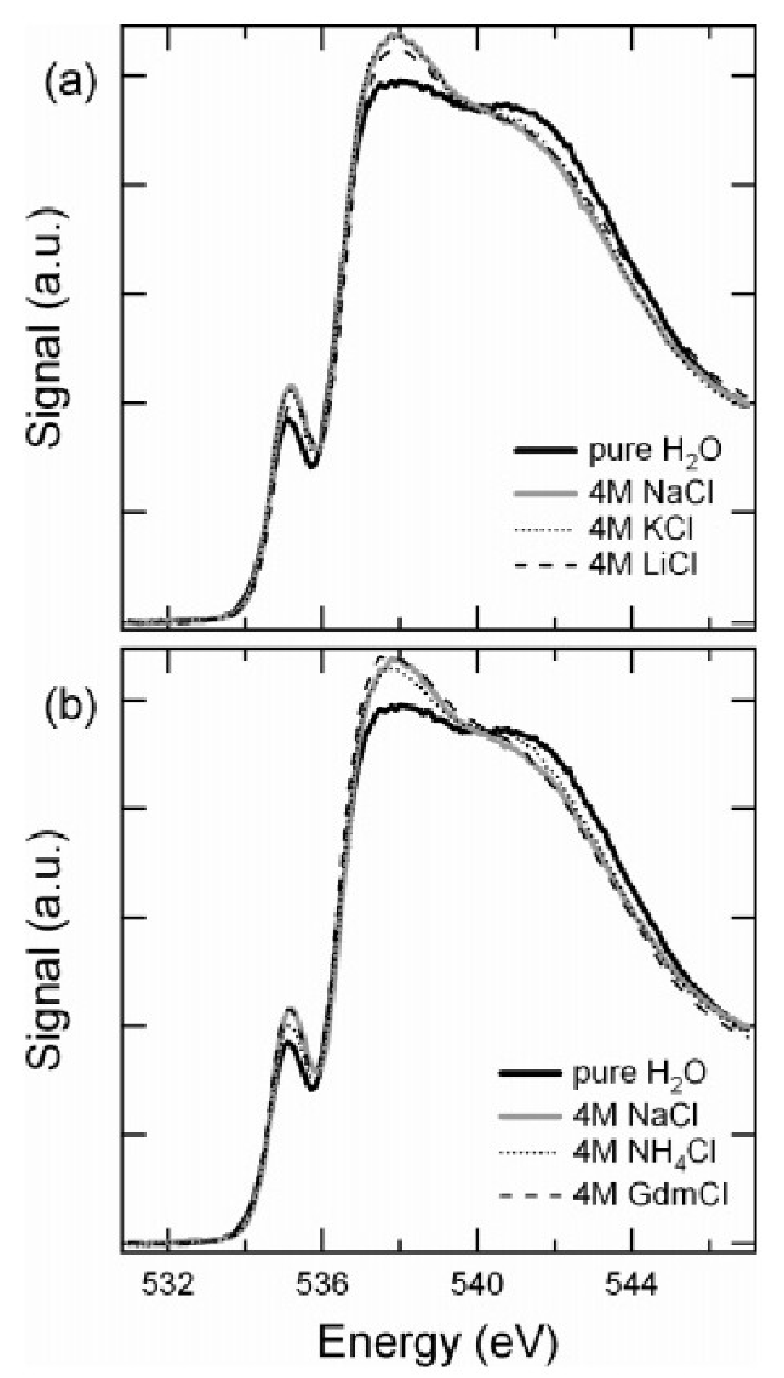
H20/D20

Soper et. al., PRL 2008



Evidence from XAS/ XES?

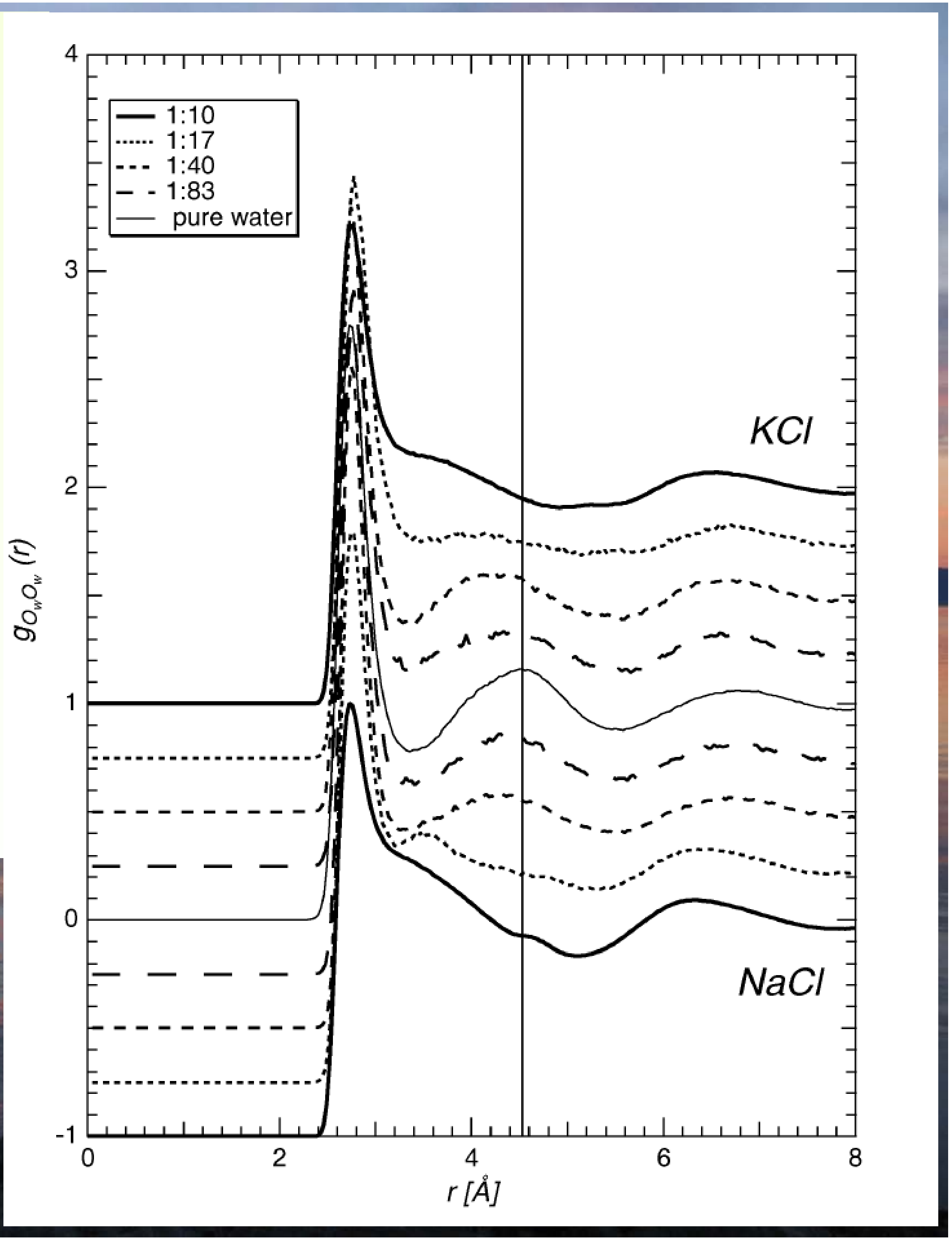
- evidence from ionic solutions



Evidence from XAS/XES?

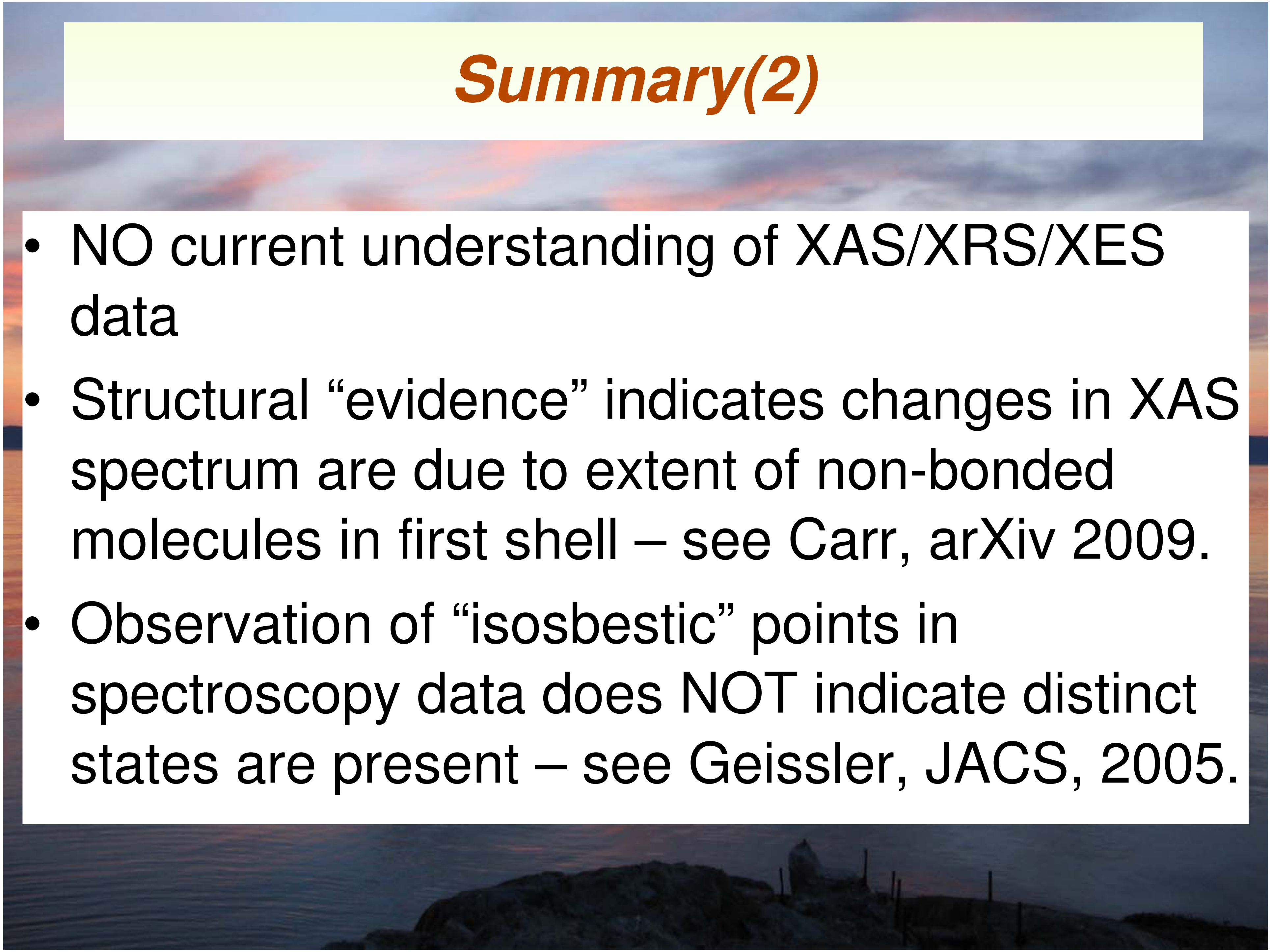
- evidence from ionic solutions

Mancinelli et. al., PCCP, 2007



Summary (1)

- A rise in scattering at small Q does NOT establish that a system has two states:
  - EPSR water simulations show SINGLE mode number fluctuations;
  - Lennard-Jonesium also shows single mode number fluctuations above the critical point.
  - Colloidal sphere model suggests a range of length scales and densities are present.
  - Cannot distinguish between heterogeneous model and homogeneous model with fluctuations.



Summary(2)

- NO current understanding of XAS/XRS/XES data
- Structural "evidence" indicates changes in XAS spectrum are due to extent of non-bonded molecules in first shell – see Carr, arXiv 2009.
- Observation of "isosbestic" points in spectroscopy data does NOT indicate distinct states are present – see Geissler, JACS, 2005.

Conclusion...

- Data presented in PNAS 2009 are highly ambiguous.
- Cannot conclude water is inhomogeneous

The ~~inhomogeneous~~ homogeneous! structure of water at ambient conditions

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Thank you!