THERMODYNAMICS OF SUPERCOOLED WATER IN SOLUTIONS

Paola Gallo, Dario Corradini and Mauro Rovere

Dipartimento di Fisica, Università Roma Tre

and INFM-CNR Democritos simulation center

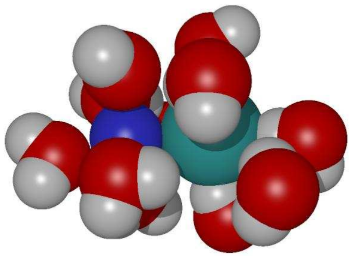
OUTLINE:

- Motivations
- The system: aqueous solution of TIP4P water and Na^+ Cl^- ions
- Thermodynamics in comparison with the bulk phase: Spinodal and TMD
- Comparison with a hydrophobic system
- Concluding remarks

ESF-FWF Conference in Partnership with LFUI
WATER INTERFACES IN PHYSICS, CHEMISTRY AND BIOLOGY: A MULTI-DISCIPLINARY APPROACH

Obergurgl, Austria, 8.12 - 13.12 2007

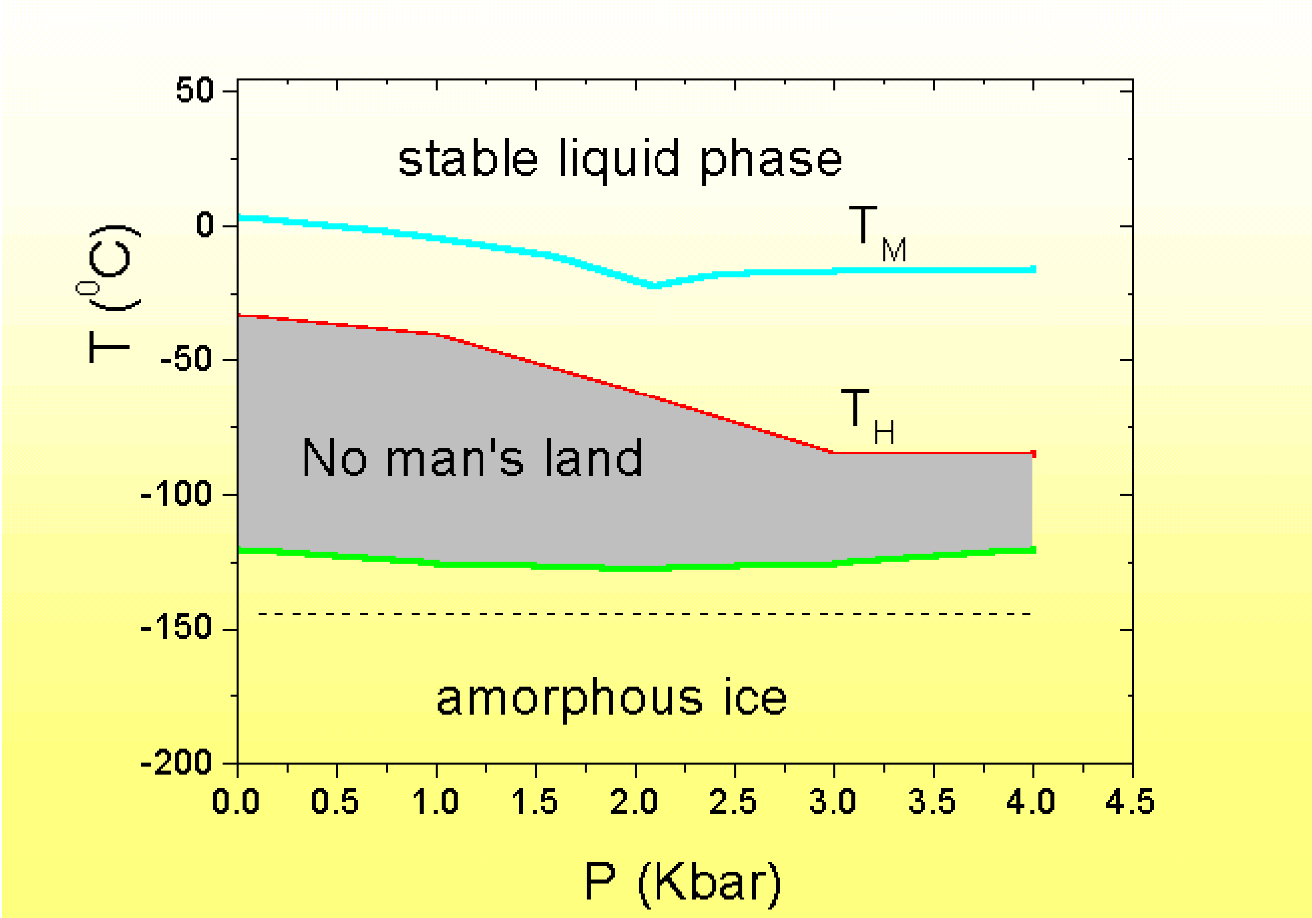
Supercooled aqueous solutions



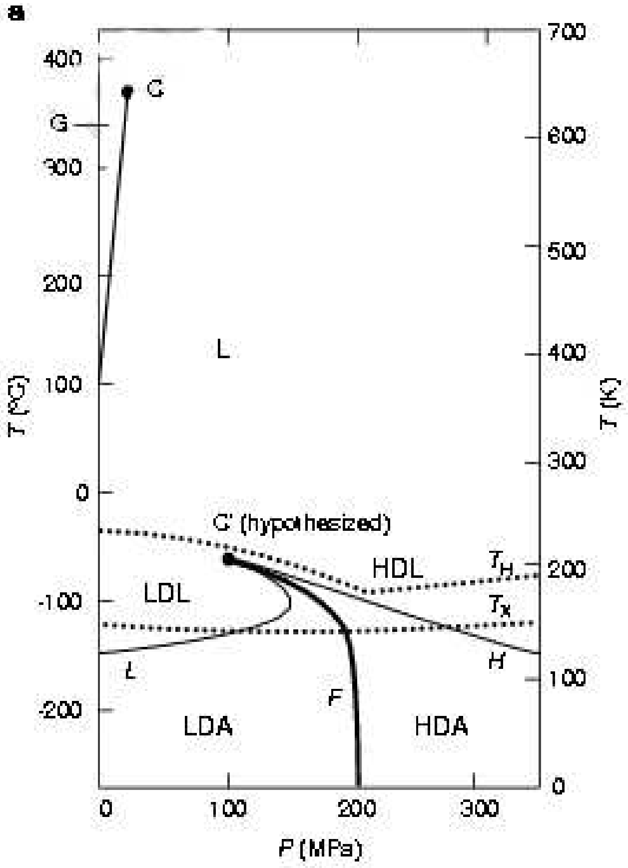
- Thermodynamics and structural properties of aqueous solutions of electrolytes are important in electrochemical and biological processes
- Properties like melting point, boiling point and viscosity are influenced by the presence of the solutes
- What happens upon supercooling?

- Cryopreservation
- Can aqueous solution help to shed light on the anomalous behaviour of water upon supercooling?

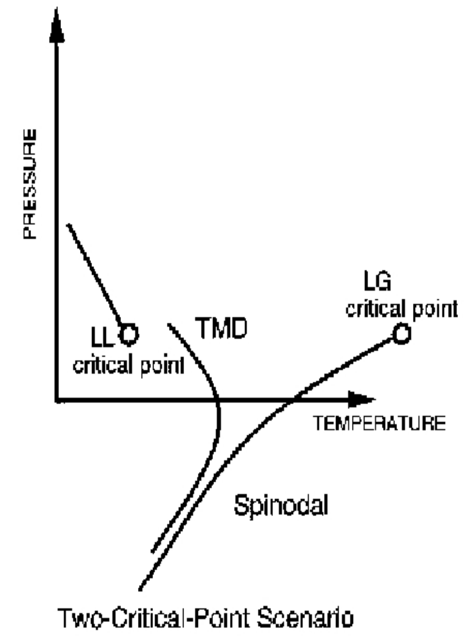
Supercooled bulk water thermodynamics scenario



Second critical point hypothesis



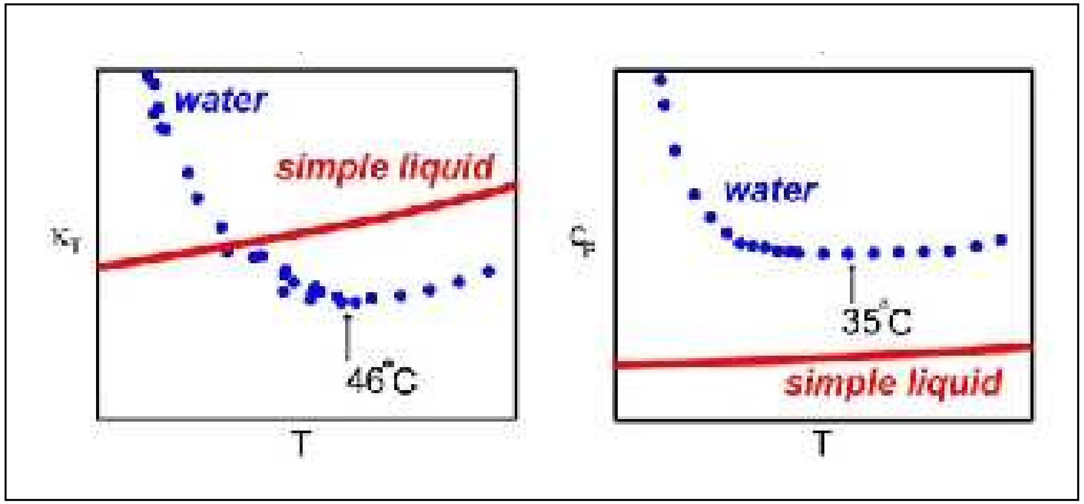
Phase diagram studies, based on extrapolation of simulated data **with several water models (ST2, SPC/E, TIP4P, TIP5P)***, ascribe the anomalous properties to the possible existence of a metastable, low temperature liquid-liquid critical point, associated with a phase transition between low-density and high density liquid phase

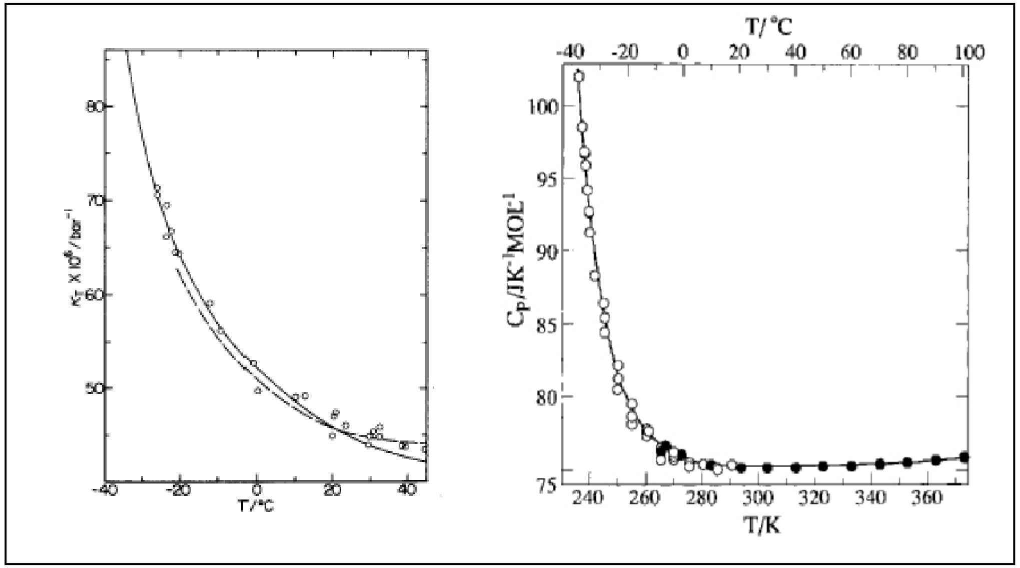


* P. H. Poole et al. Nature (1992)
S. Harrington et al. P. R. L. (1997); F. Sciortino et al. P. R. E. (1997); H. Tanaka et al. Nature (1996); M.Yamada et al. P. R. L. (2002); Brovchencko et al. JCP (2005).

Water anomalies

- **THE ISOTHERMAL COMPRESSIBILITY and THE ISOBARIC HEAT CAPACITY** increase markedly with decreasing temperature

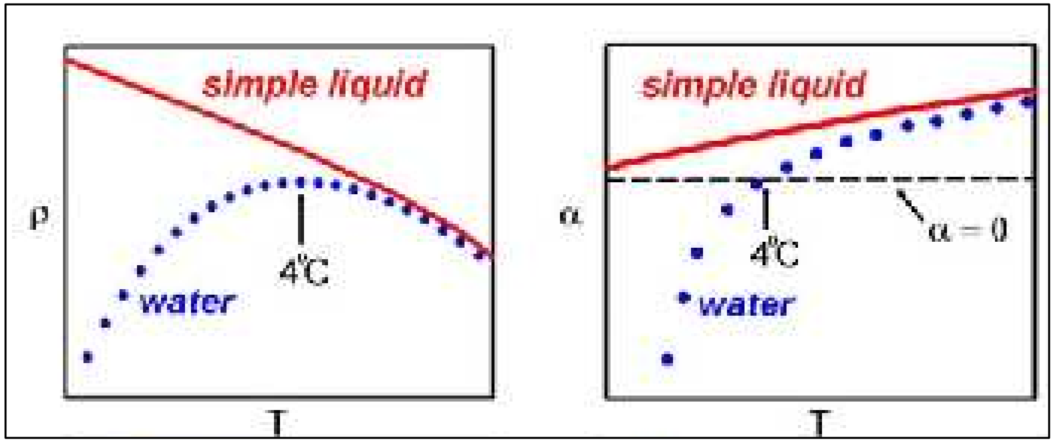


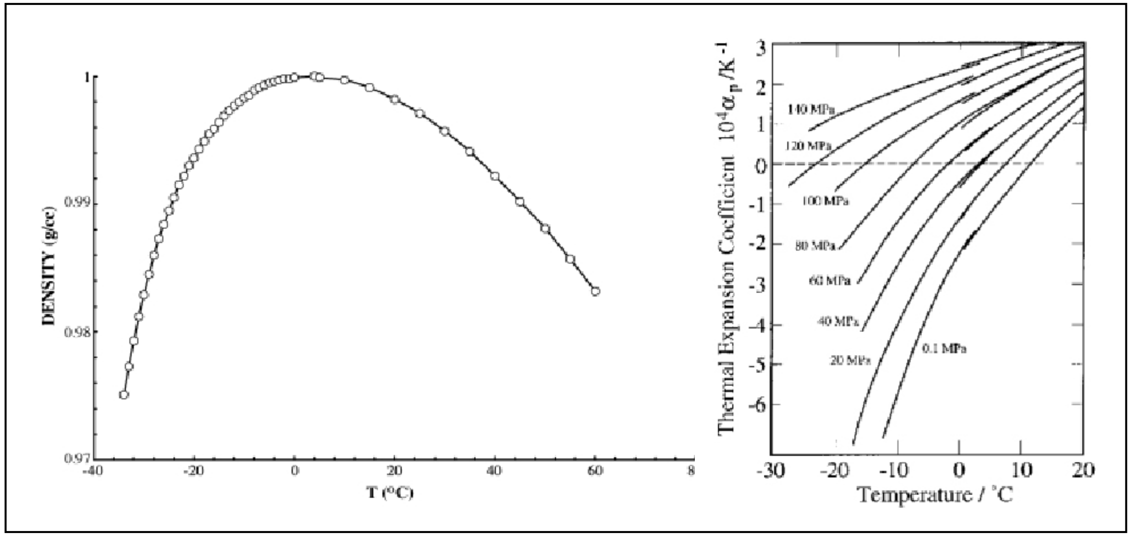


Experimental measurements

Water anomalies

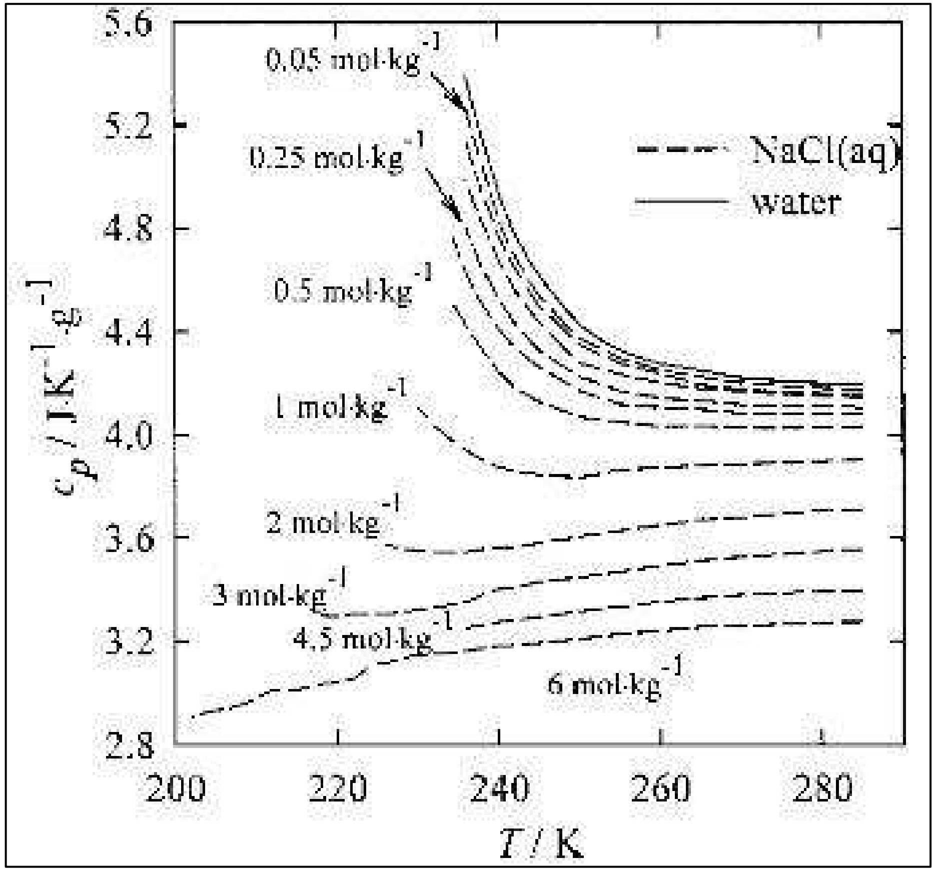
- **THE DENSITY (ρ)** of supercooled water shows a maximum value (TMD). (4 C AT 0.1 MPa).
- **THE THERMAL EXPANSION COEFFICIENT (α)** vanishes at the same temperature-

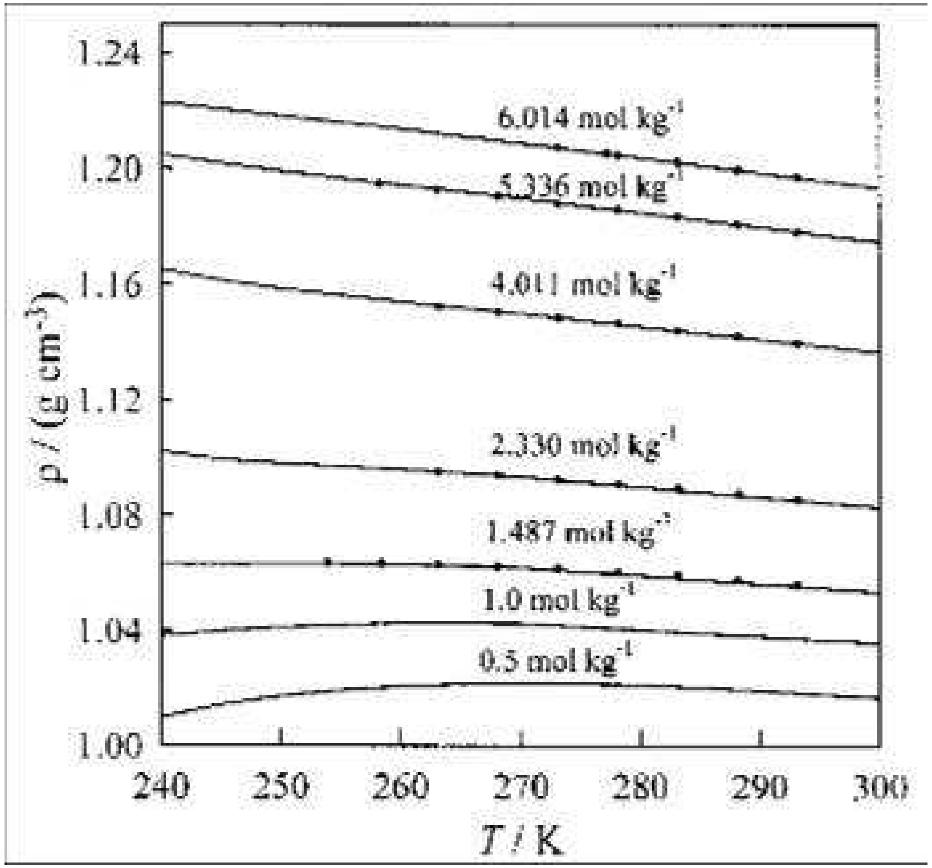




Experimental measurements of supercooled water's density and its pressure derivative.
Application of pressure displaces the anomalies to lower temperatures.

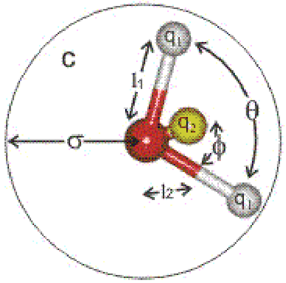
Aqueous solution NaCl(aq): experimental results





D. G. Archer and R.W. Carter J. Phys. Chem. B (2000)

MD simulations details: bulk



Water model potential TIP4P:

l_1=0.9572 Å l_2=0.15 Å

q_1=0.52e θ=104.52 ϕ=52.26 (Ewald sums)

σ=3.15365 Å ε=0.6480 kJ/mol

256 water molecules

Temperatures ranging from 500 to 210 K

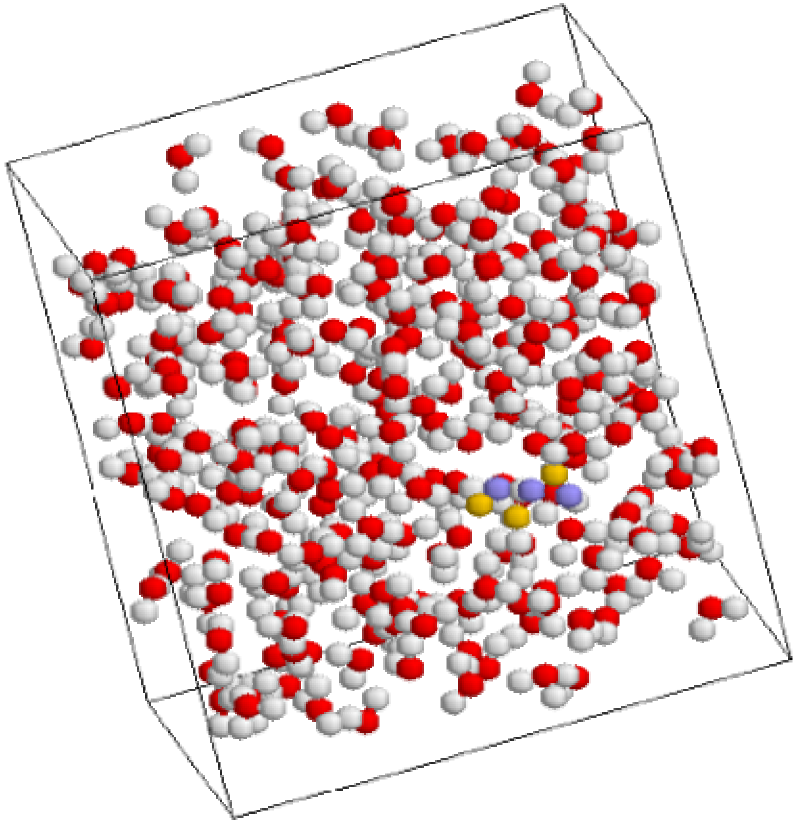
Longest equilibration/production run 10 ns

Ensemble NVT Berendsen

Timestep 1fs

ρ (gr/cm³)	L (Å)
1.05	19.388
1.00	19.710
0.98	19.839
0.95	20.046
0.90	20.410
0.87	20.650
0.85	20.811
0.83	20.977
0.80	21.236

MD simulations details: aqueous solution of water and Na^+ Cl^-



$\rho\,(\mathrm{g/cm^3})$	$\mathrm{L}(\text{Å})$
1.05	19.489
1.025	19.641
0.98	19.943
0.95	20.151
0.90	20.517
0.87	20.750
0.85	20.911
0.80	21.338

$$N_{H_2O} = 250\,;\; N_{Na^+} = 3\,;\; N_{Cl^-} = 3$$

$$c = 0.67\,\frac{mol}{kg}$$

Temperatures ranging from 500 to 210 K

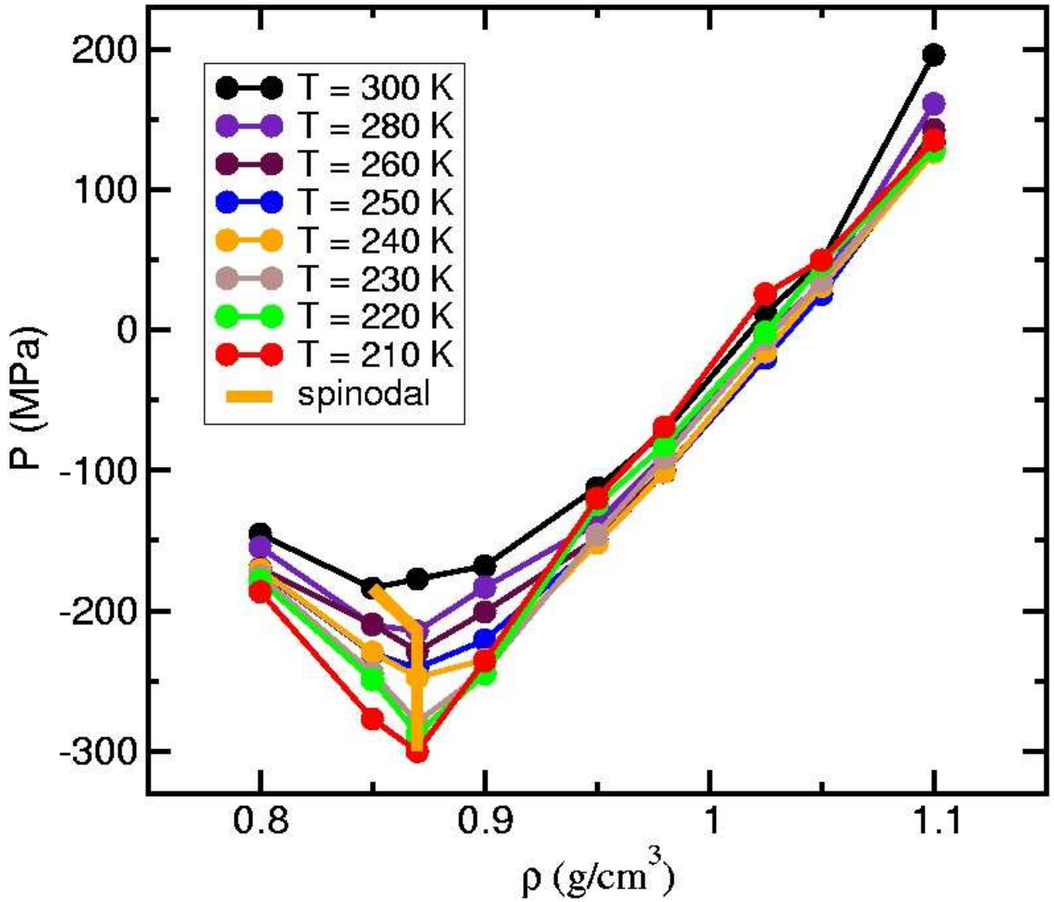
Longest equilibration/production run 10 ns

Ensemble NVT Berendsen

Timestep 1fs

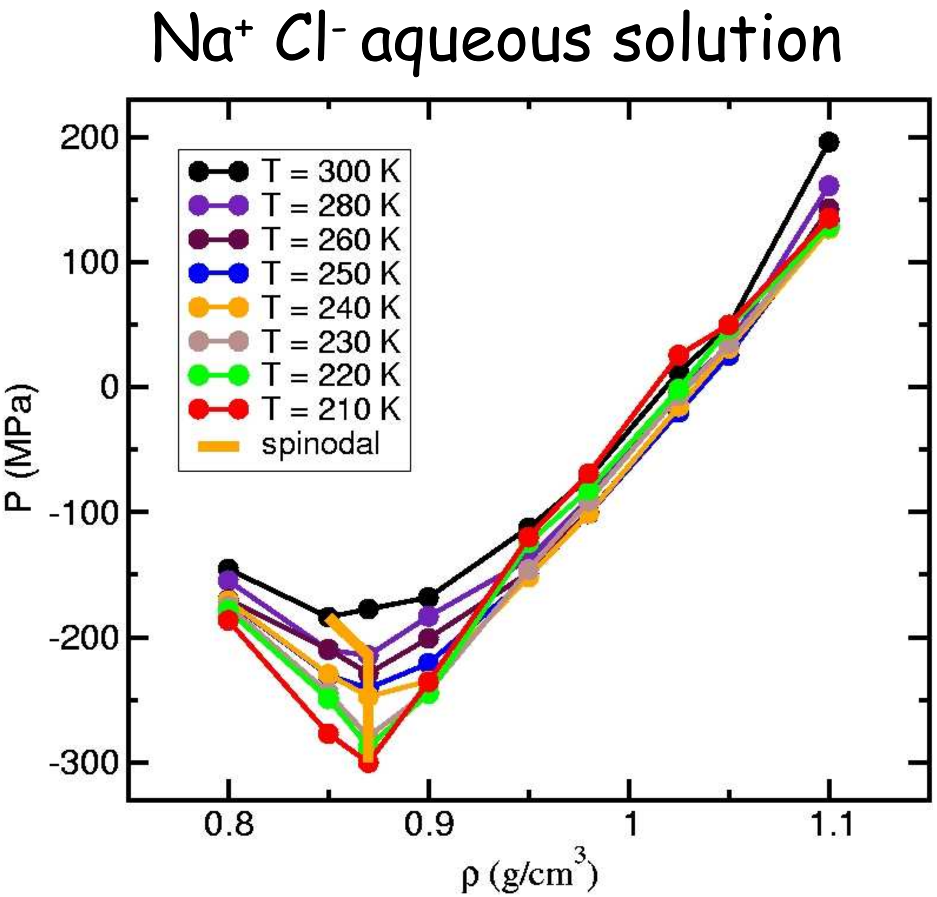
Water-ion and ion-ion potential taken from B.N. Pettitt, P. J. Rossky, JCP (1984) + S. Koneshan, J. C. Rasaiah, JCP (2000)

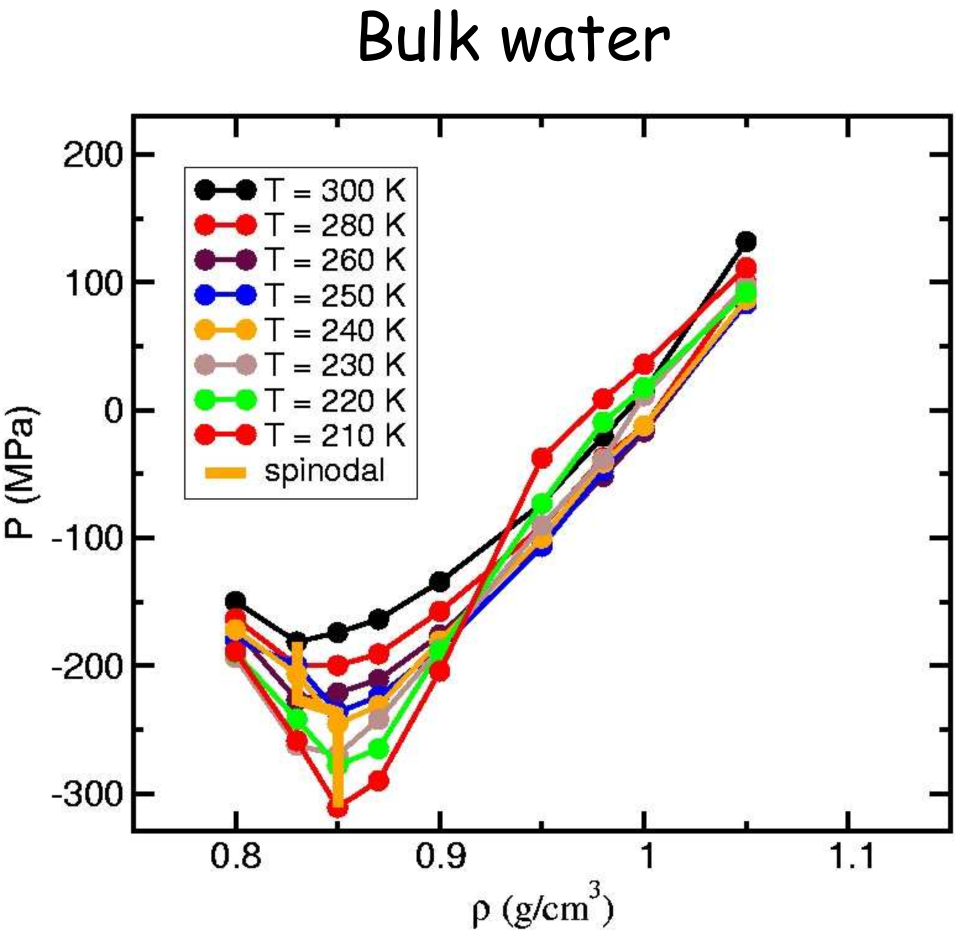
Aqueous solution: thermodynamics



- The boundary between metastable and unstable states is the spinodal line.
- States for which K_T>0 are either stable or metastable, while states for which are K_T<0 unstable
- K_T, the coefficient of isothermal compressibility, is proportional to the slope of isotherms trough the relation $1/K_T \sim -V(dP/dV)$.
- **the liquid spinodal occurs at the minimum of an isotherm of P versus ρ.**

Bulk water and aqueous solution: thermodynamics

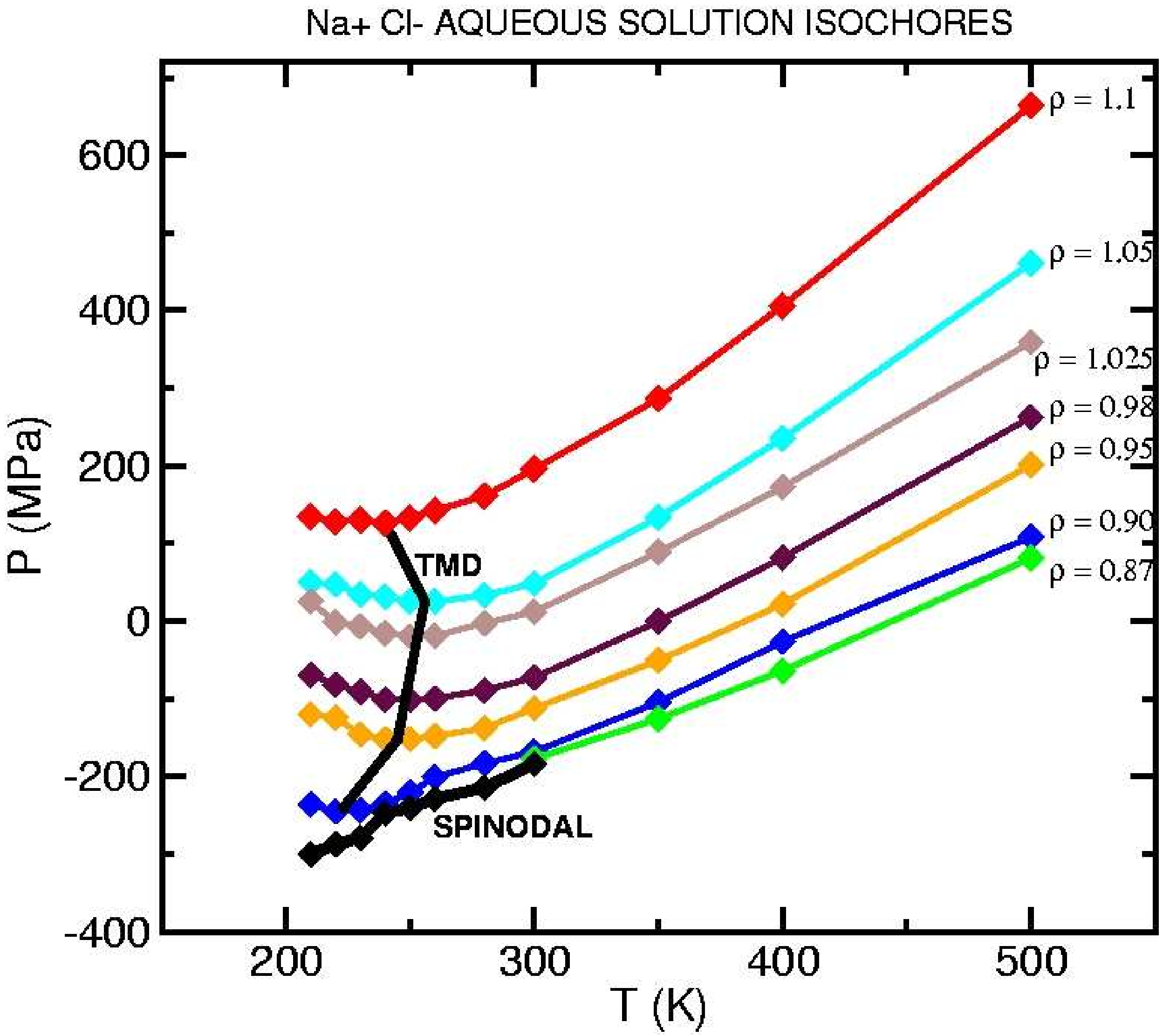




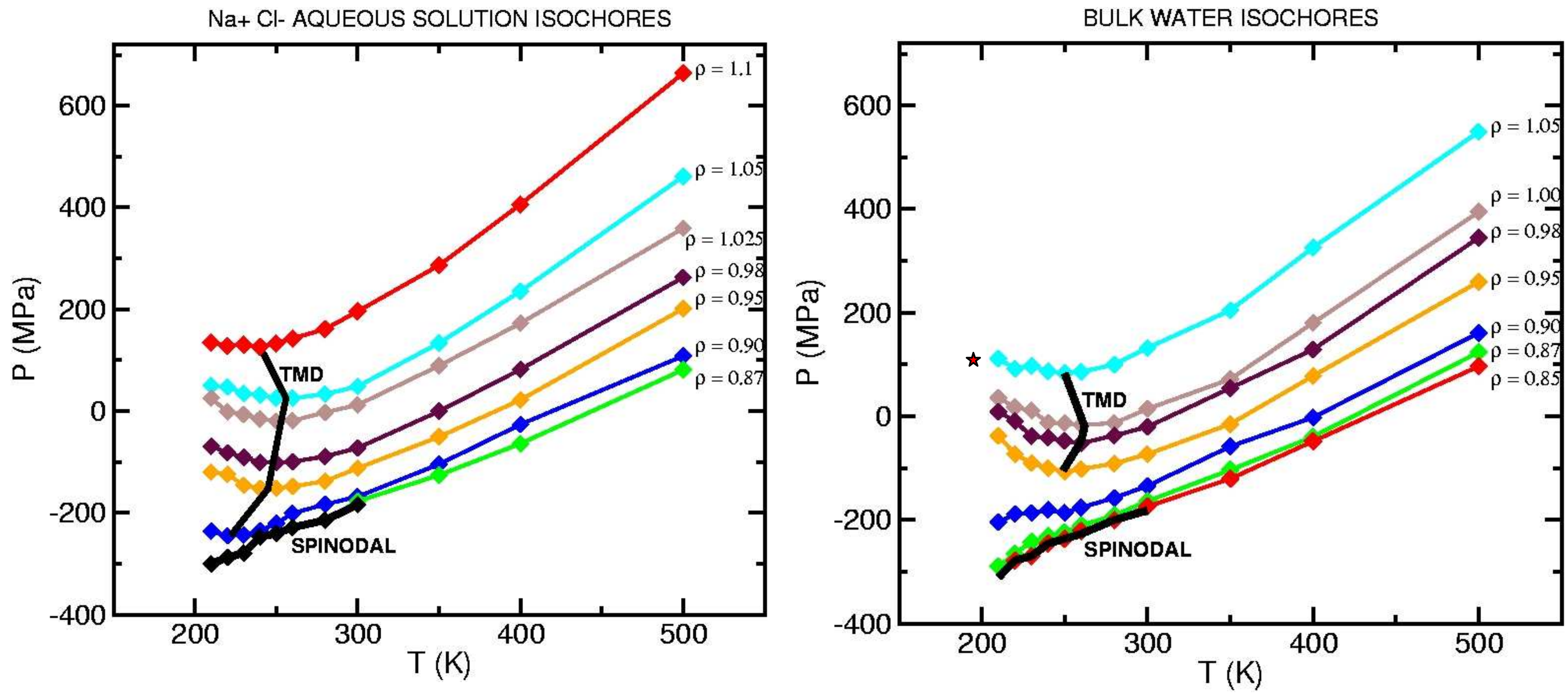
The change of curvature in the low temperature isotherms happens when the system is approaching from above in T a critical point (second).

Poole et al. Nature 1992; Poole et al. PRE 1993

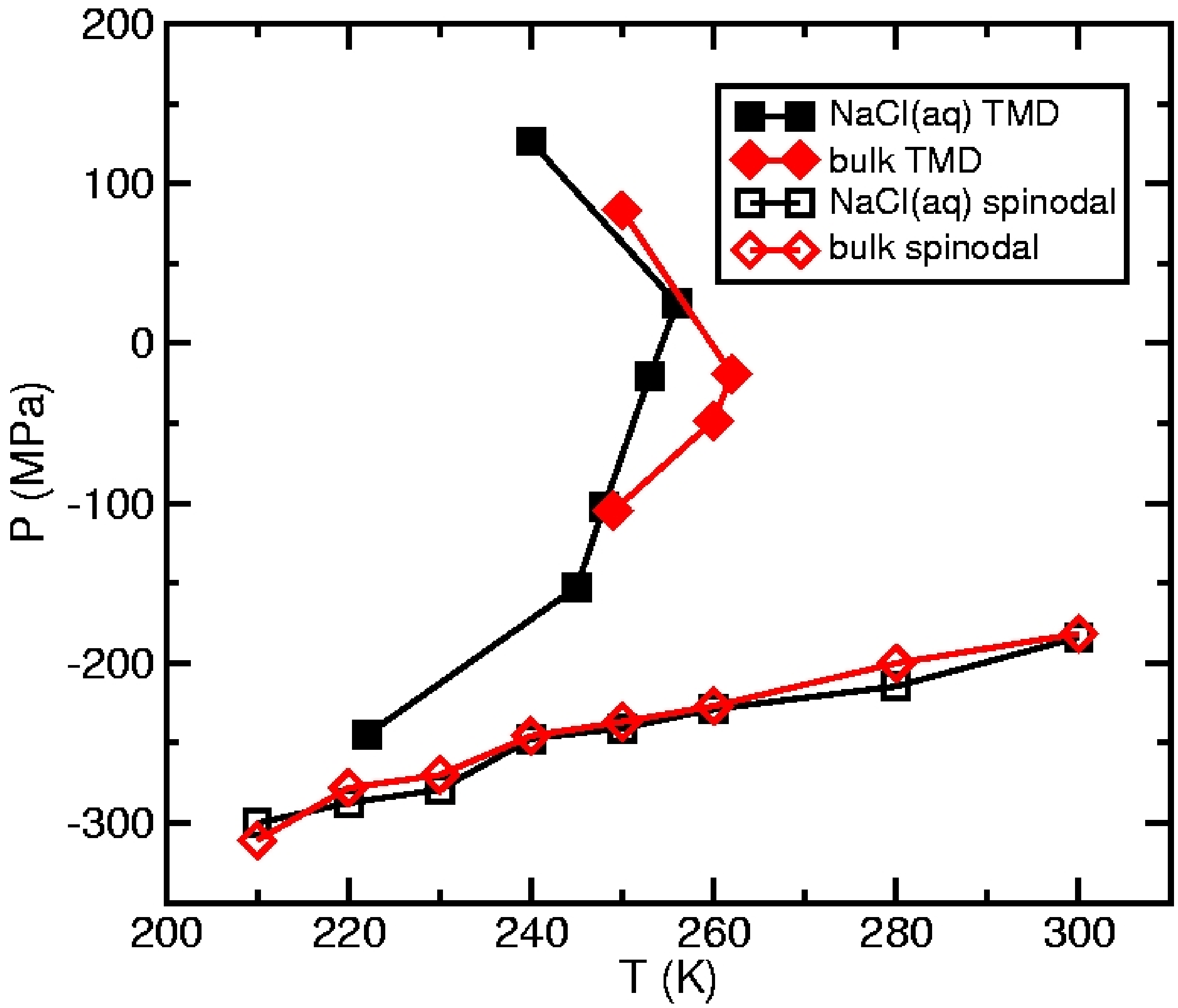
Aquous solution: thermodynamics



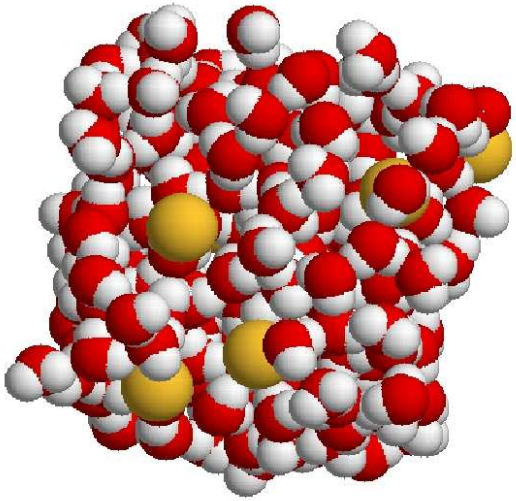
Bulk water and aqueous solution: thermodynamics



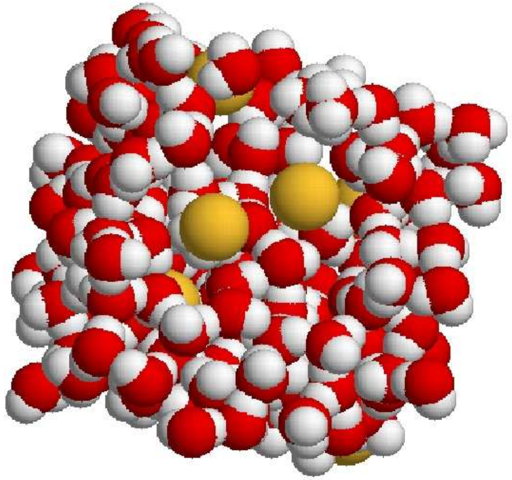
Bulk water and aqueous solution: thermodynamics



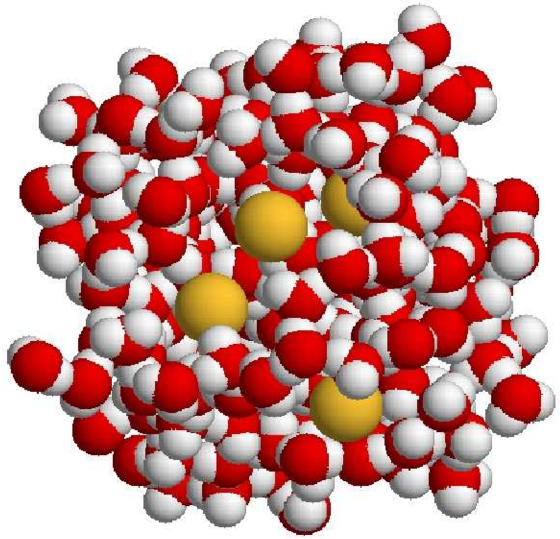
Hydrophobic confinement: system



T=300 ρ= 0.85



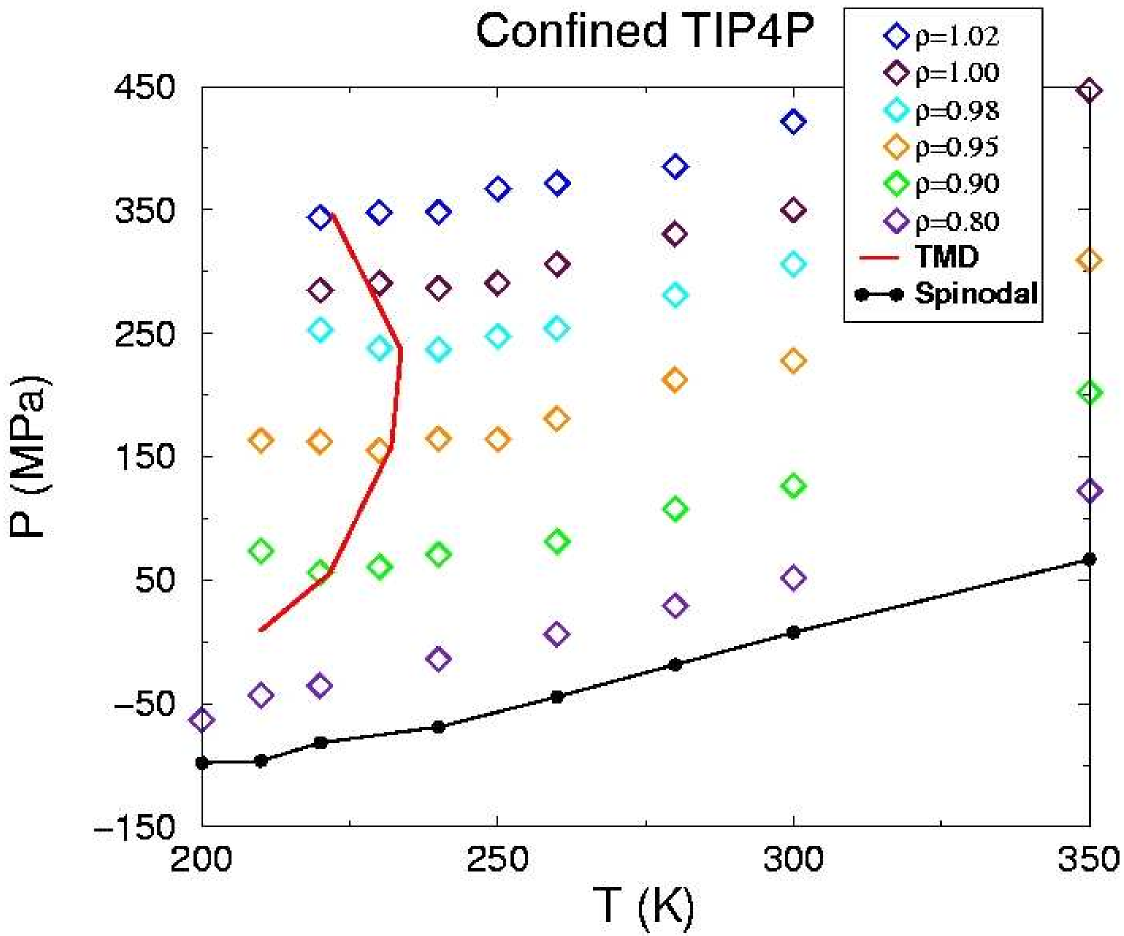
T=300 ρ= 0.75



T=220 ρ= 0.85

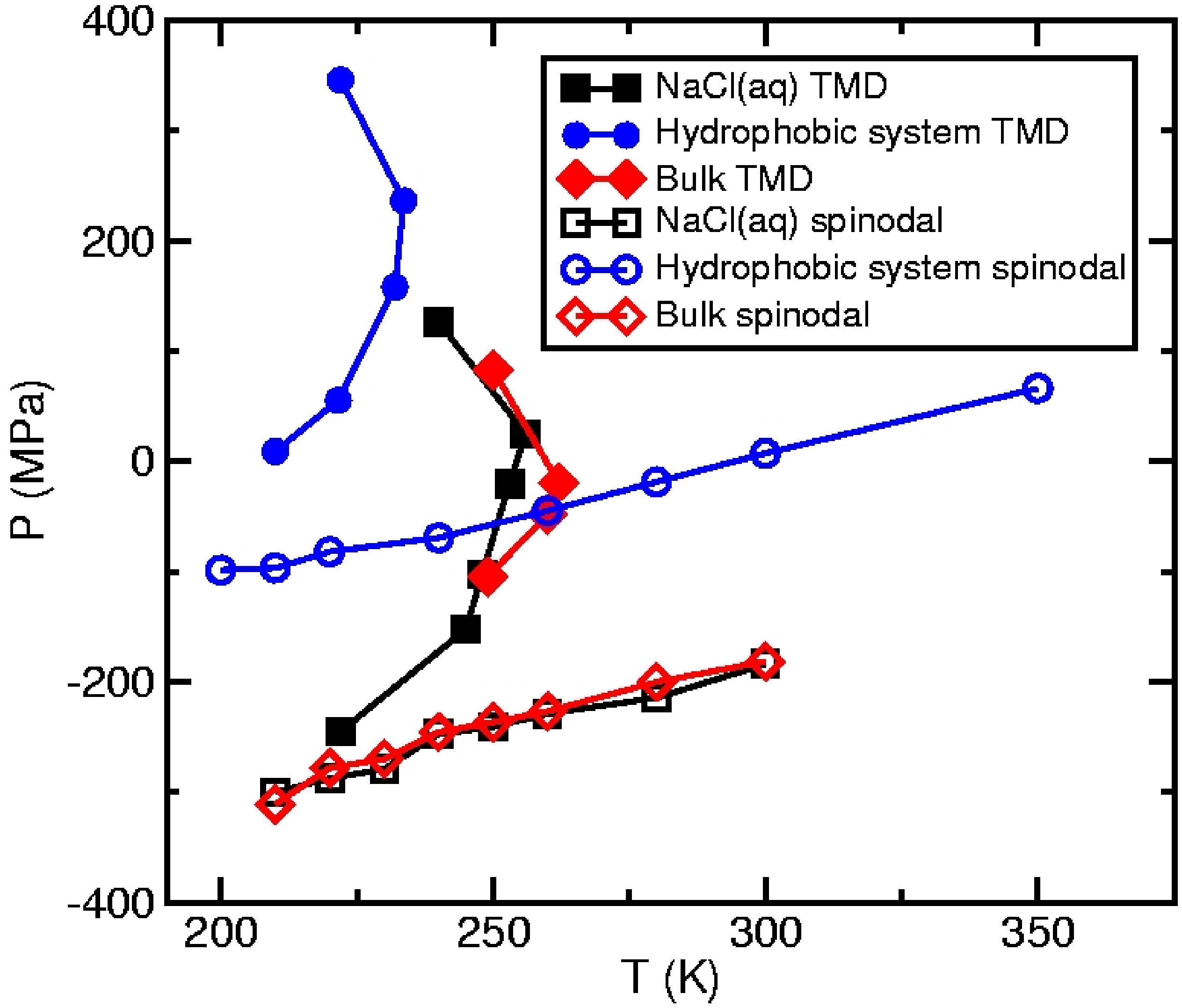
Model system: TIP4P water embedded in a rigid off lattice matrix of 6 soft spheres

Confined system: thermodynamics

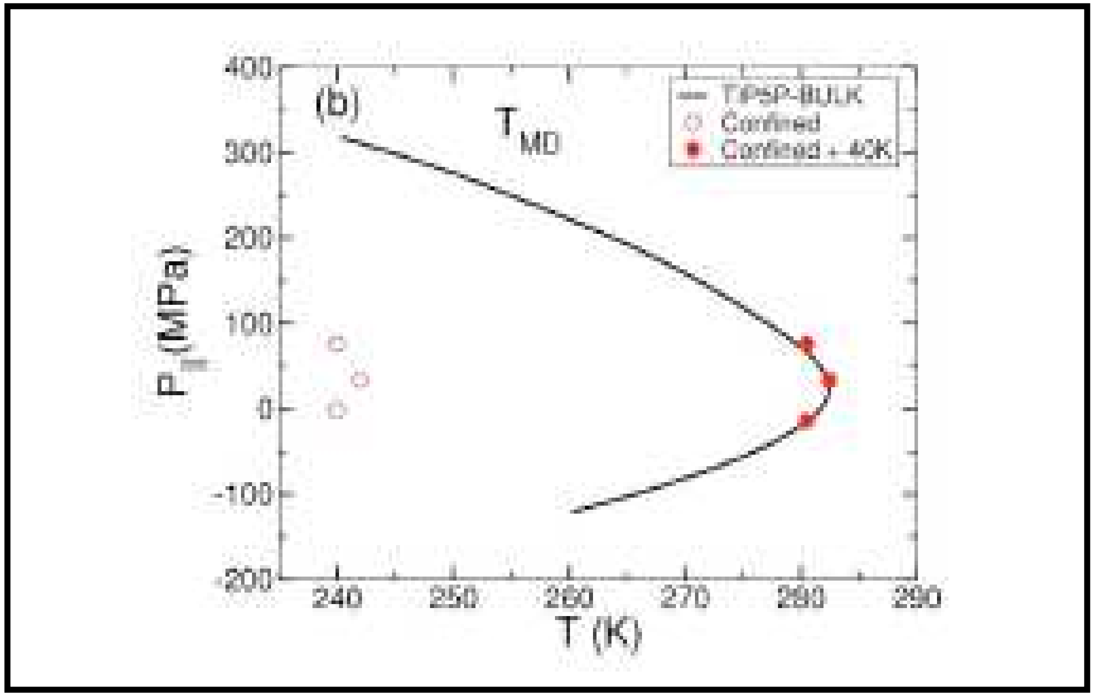


P. Gallo and M. Rovere, Phys. Rev. E (in press).

Bulk water and aqueous solution and hydrophobic system: thermodynamics



TIP5P water confined between hydrophobic plates separated by 1.1nm



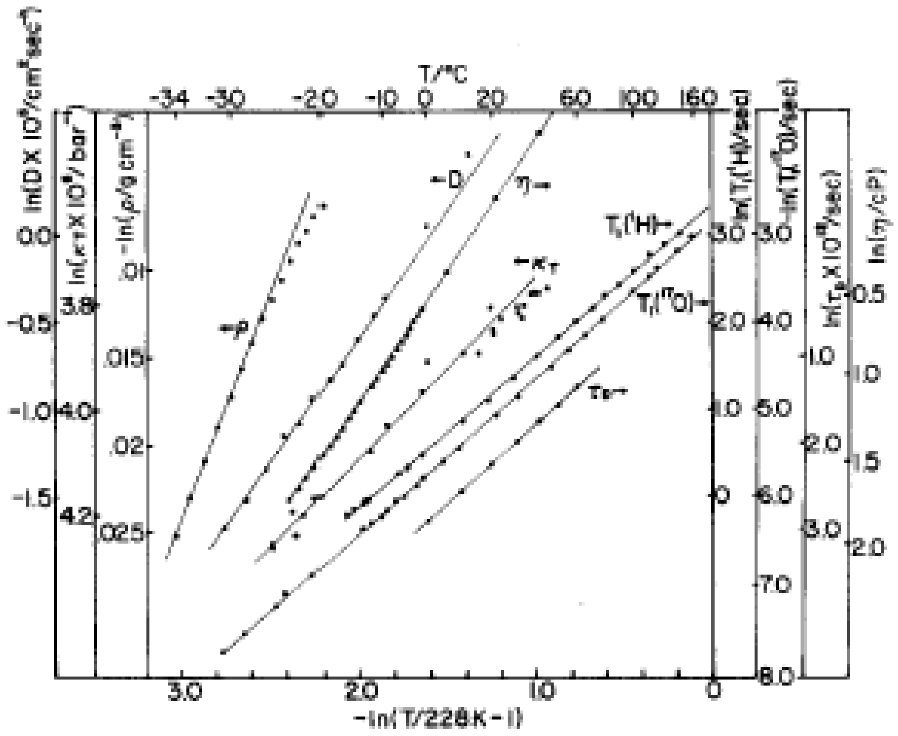
[P. Kumar, S. Buldyrev, F.W. Starr, N. Giovanbattista and H.E. Stanley PRE 72, 051503 (2005)]

Conclusions

- The same thermodynamic scenario of the bulk is found: the spinodal line remains also identical while the TMD changes in shape: broadens and slightly shifts toward lower temperatures. No shift in pressures can be seen.
- Water in presence of a hydrophobic solute shows a shift of TMD and spinodal both toward lower temperatures and higher pressures.
- Signatures of the existence of a second critical point are present (change of curvature in the isotherms).
- Future studies to understand where the critical point moves (we guess to higher densities). Experiments in silica nanopores indicate it to be supposedly located at 200 K and 160 MPa (Liu, Chen, Faraone, Yen, Mou PRL (2005)).

Water anomalies

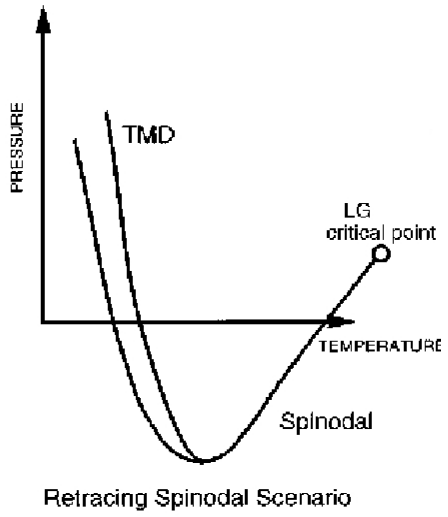
The lowest temperatures at which quantities are measurable is, up to now, T=-38 C at 1 bar, due to the strong tendency of metastable water to crystallise.
If they are extrapolated below this temperature
<u>they appear to diverge at Ts~-45 C</u>

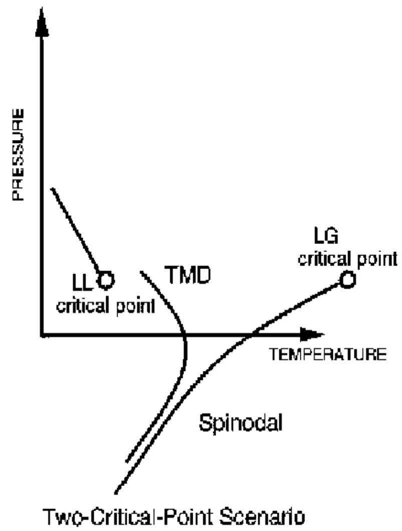


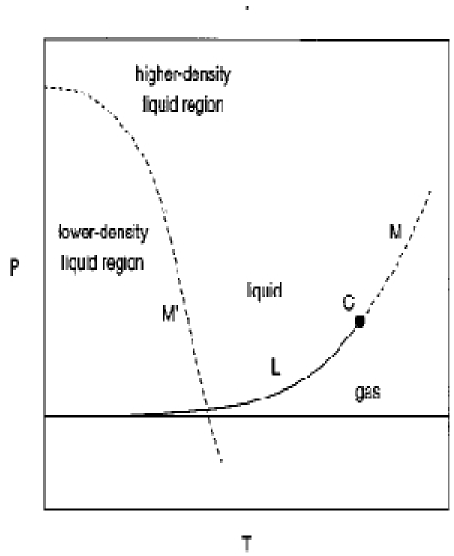
H. Kanno,C.A. Angell J.Chem.Phys.70 4008(1979)

A coherent theory of the thermodynamic and transport properties of supercooled water does not yet exist, also due to the difficulties encountered in experiments.

Supercooled bulk water thermodynamics scenario







Retracing spinodal hypothesis

[R.J.Speedy, J. P. C. (1982)]

Second critical point hypothesis –
[P.H.Poole et al. Nature (1992)]

Singularity free –

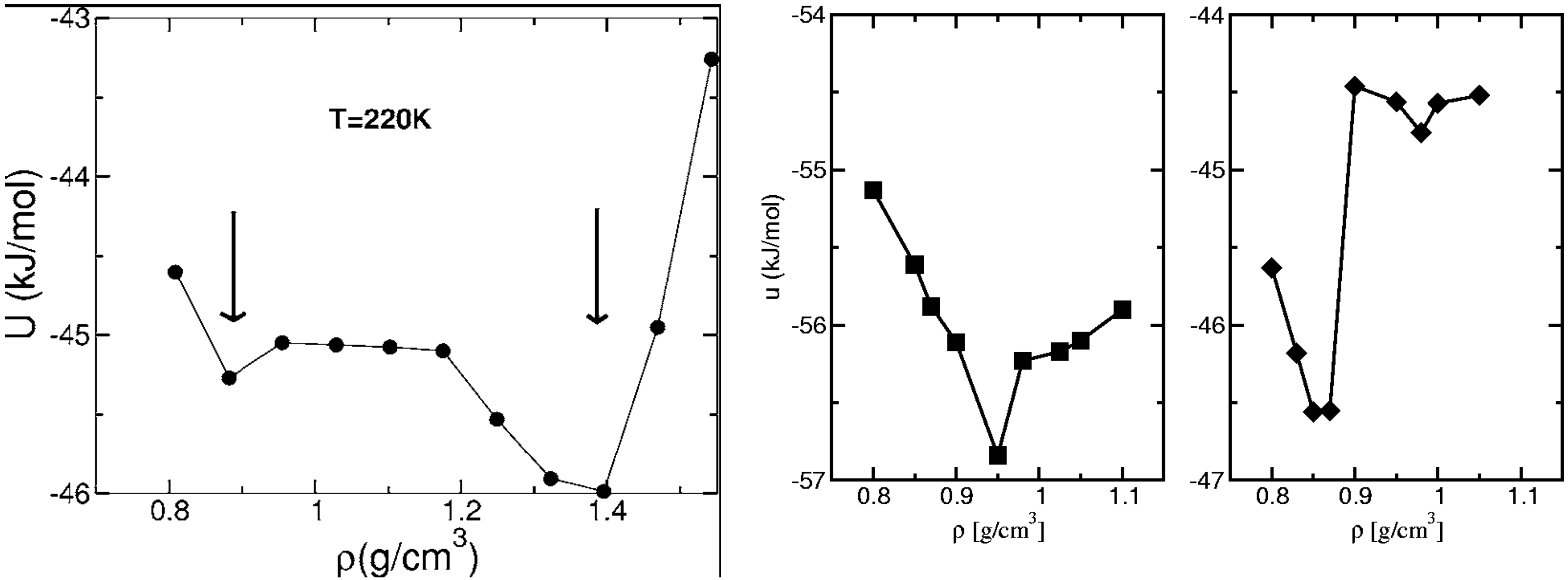
[S.Sastry et al. P.R.E (1996)]

Bulk water and aqueous solution: thermodynamics

Water confined in hydrophobic plates

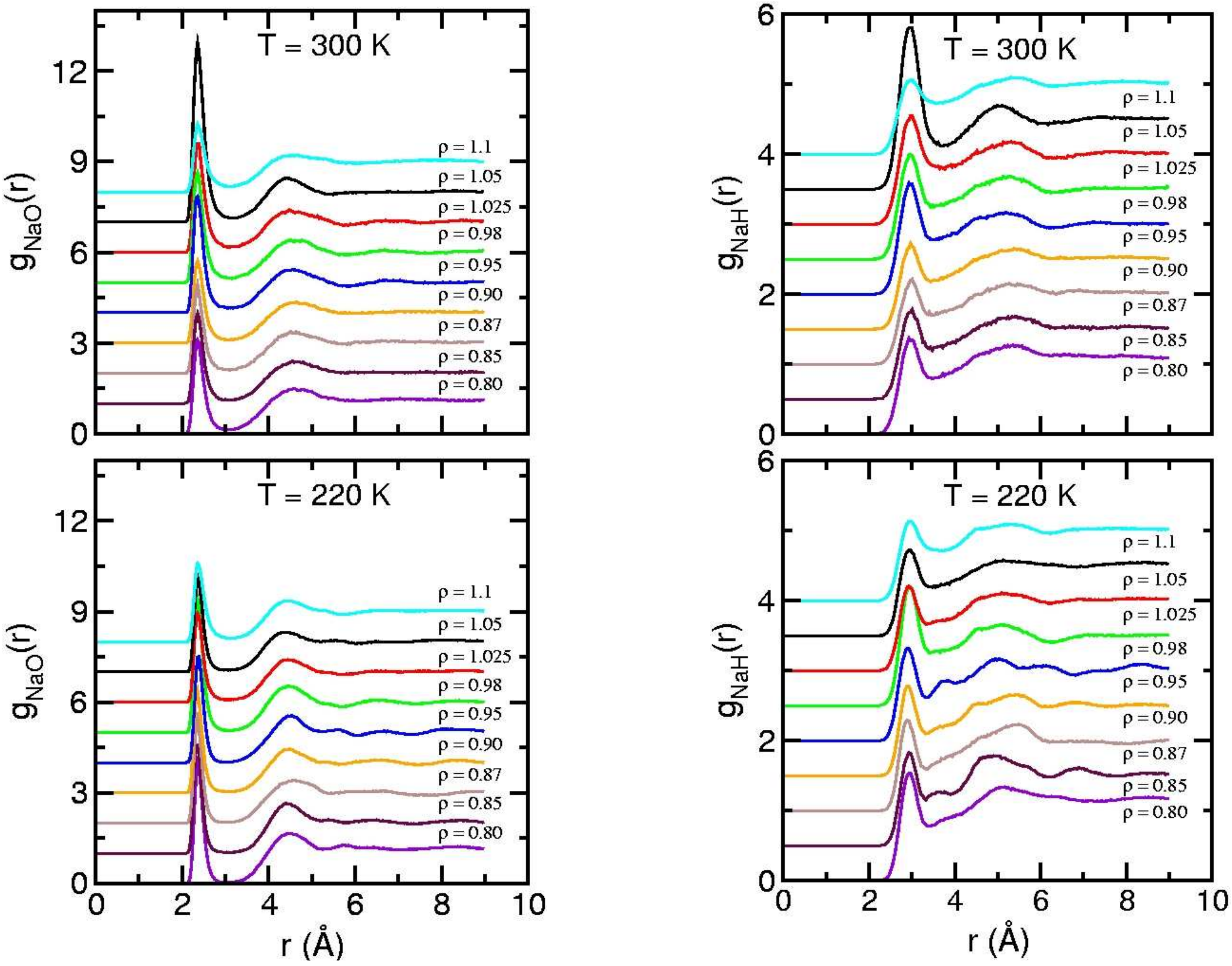
NaCl(aq)

Bulk



[P. Kumar et al. PRE 72, 051503 (2005)]

Radial Distribution Functions ion-water



Radial Distribution Functions ion-water