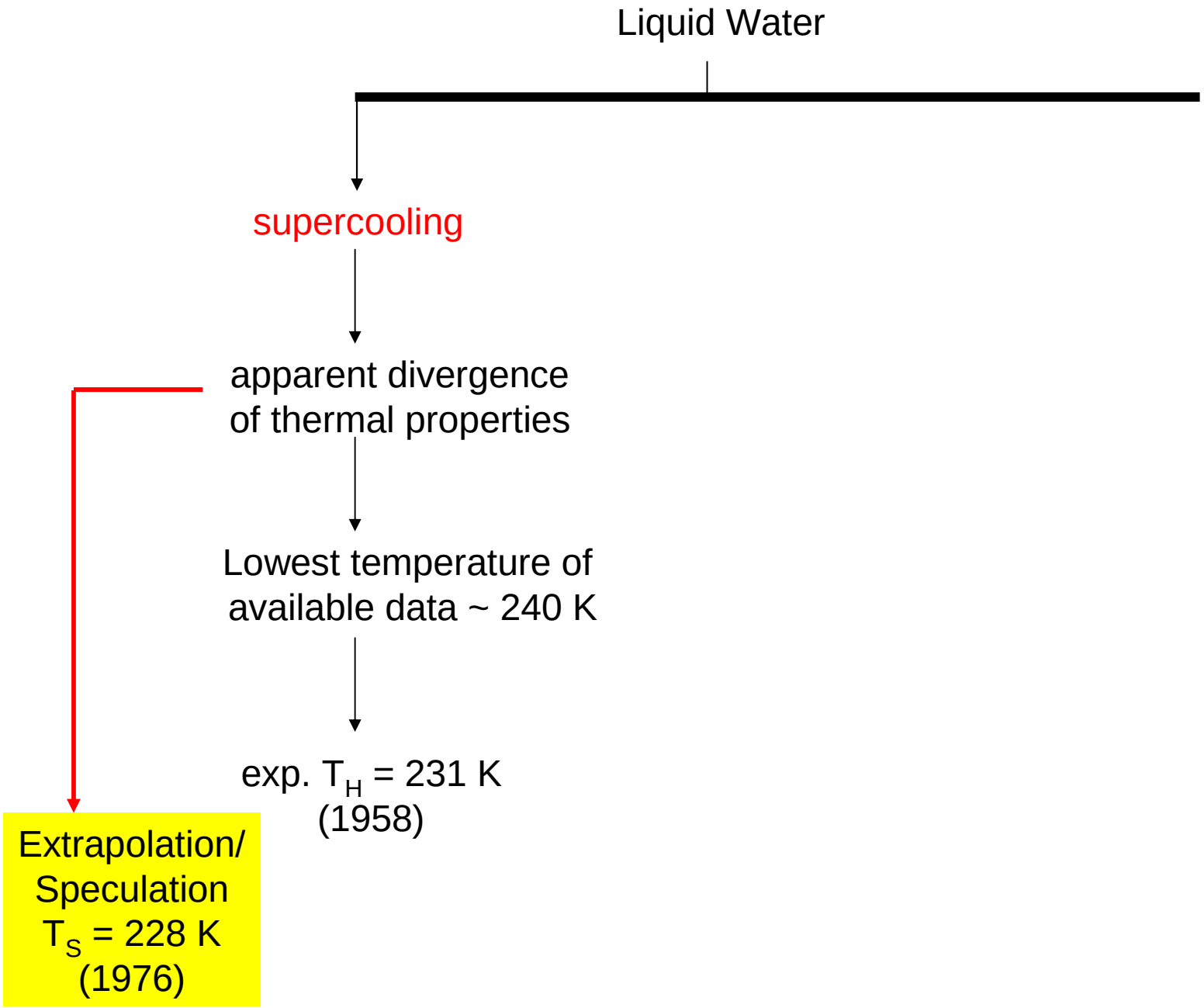
Study of the dynamics of hydrogen bonds in water and consequences for the unusual behaviour of supercooled water

José Teixeira and Stéphane Longeville

ESF-FWF Conference, Obergurgl, Austria, 2007


Liquid Water
supercooling
apparent divergence
of thermal properties
Lowest temperature of
available data ~ 240 K
exp. T_H = 231 K
(1958)
Extrapolation/
Speculation
T_S = 228 K
(1976)

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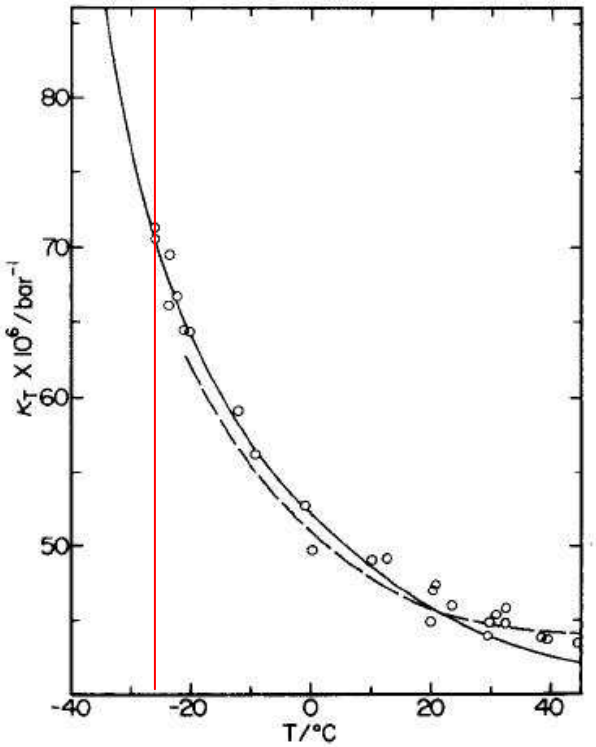

FIG. 2. Compressibility of water in normal and supercooled states. Dashed line is polynomial extrapolation by Kell, (Ref. 13) of data from above 0 °C. Solid line is plot of Eq. (2) for parameters given in text.

R. Speedy and C.A. Angell
J. Chem. Phys. **65**, 851 (1976)

Liquid Water

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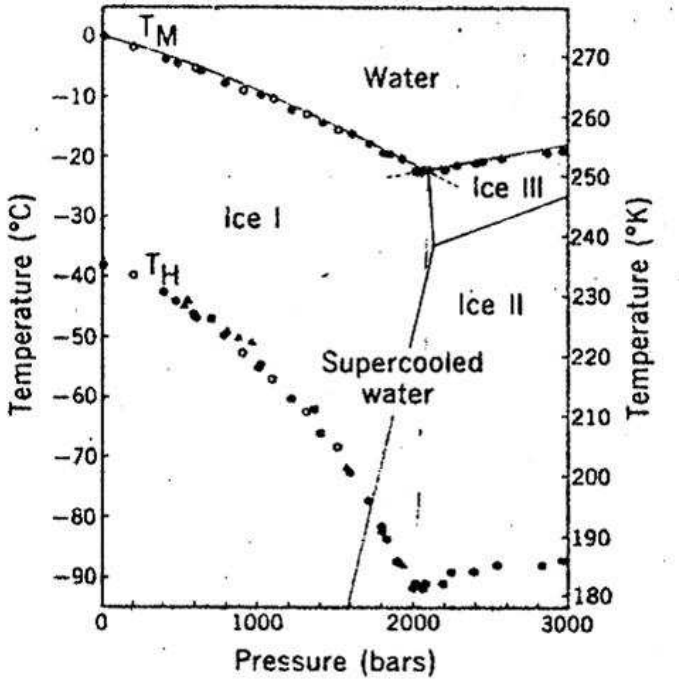
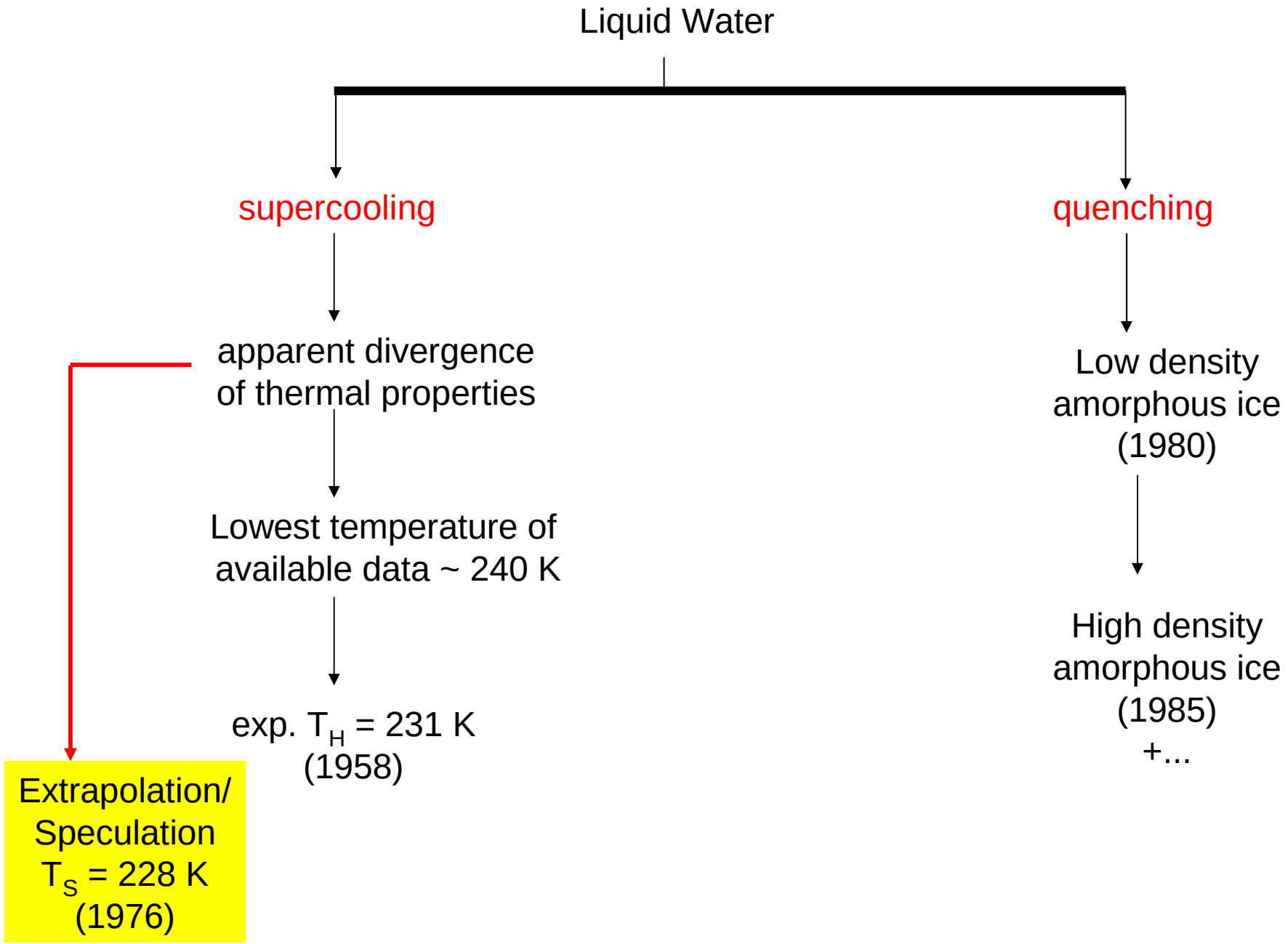


H. Kanno, R.J. Speedy and C.A. Angell
*Science **189**, 880 (1975)*


Liquid Water
supercooling
quenching
apparent divergence of thermal properties
Low density amorphous ice (1980)
Lowest temperature of available data ~ 240 K
High density amorphous ice (1985) +...
exp. T_H = 231 K (1958)
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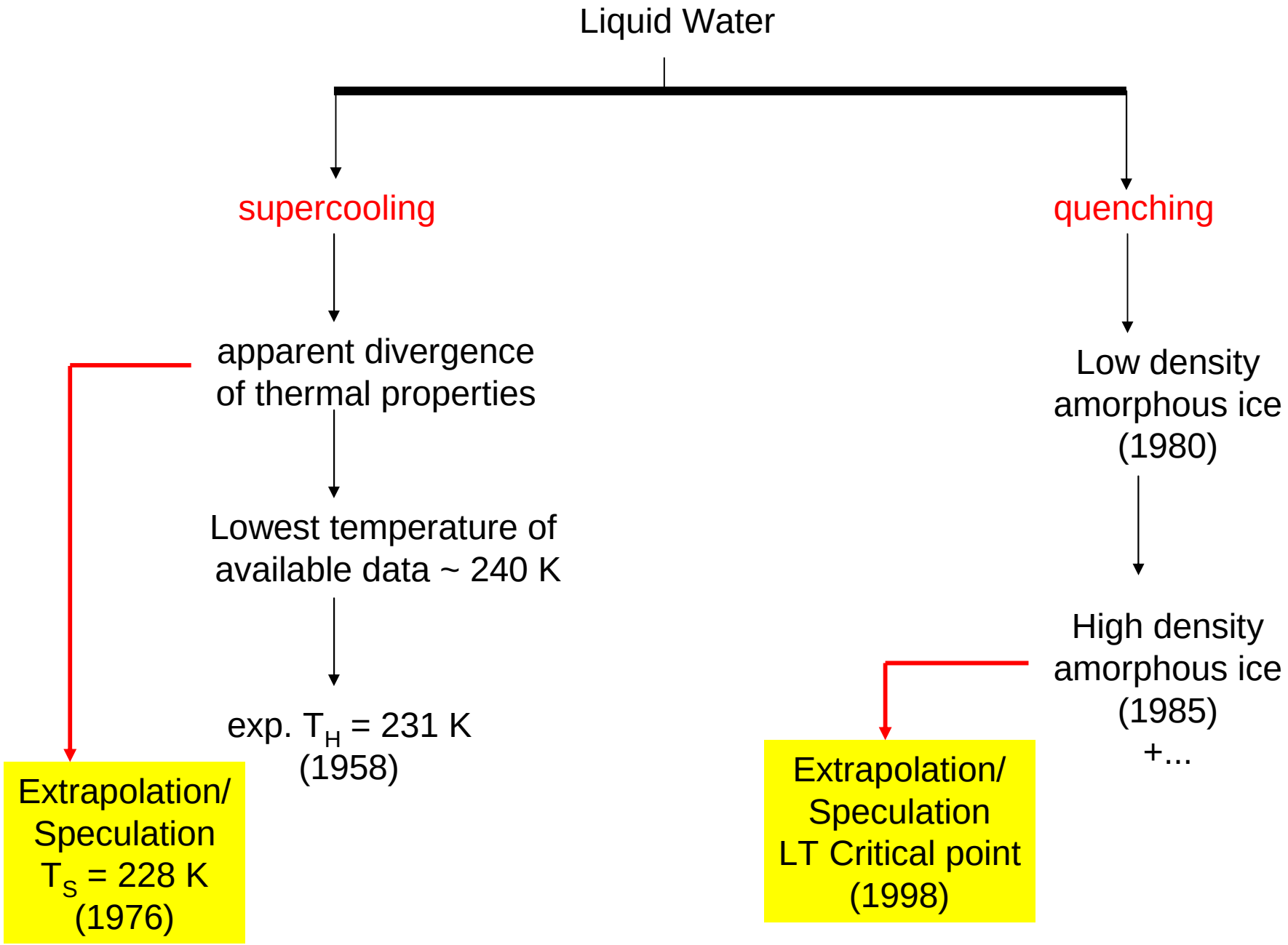
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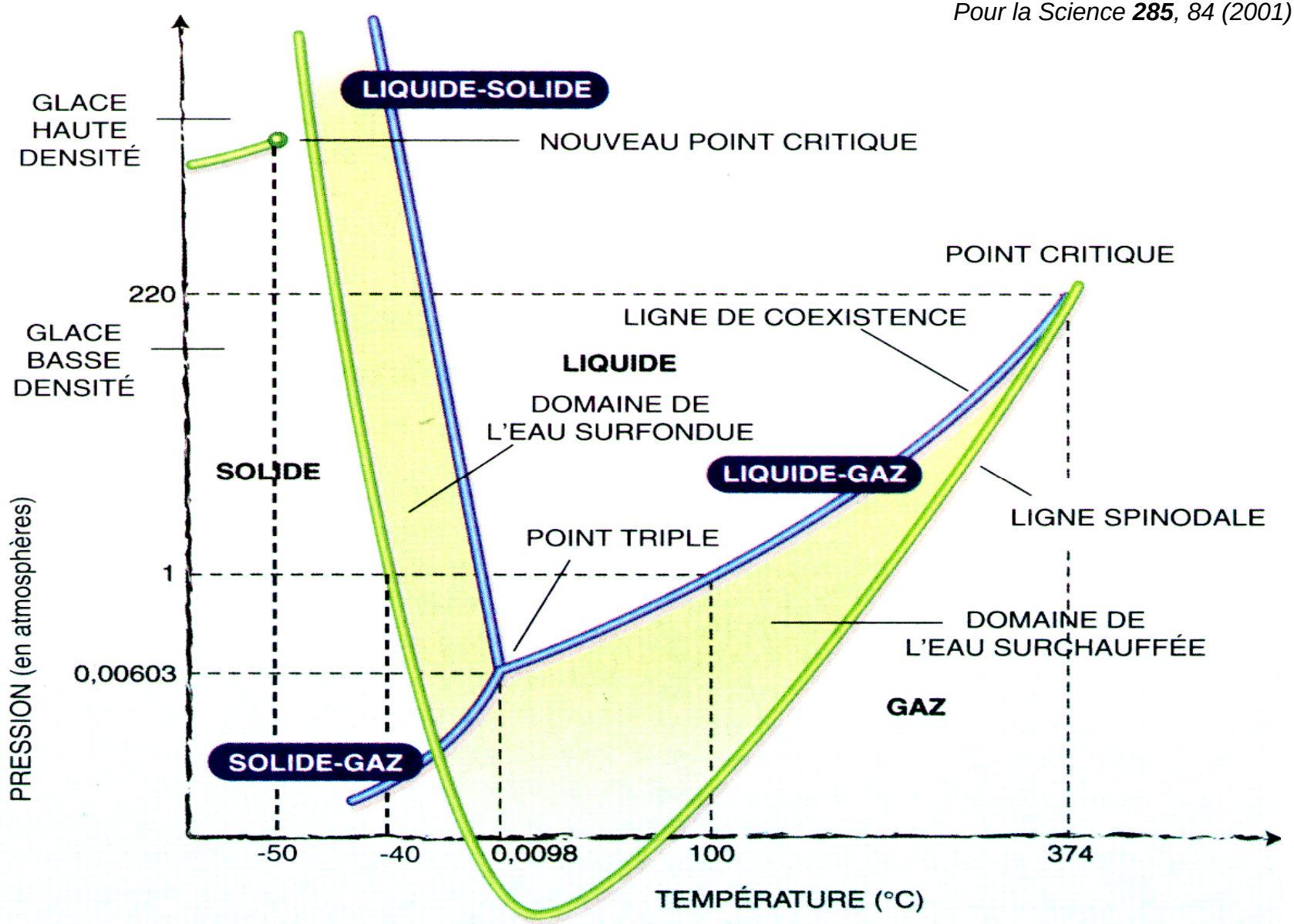
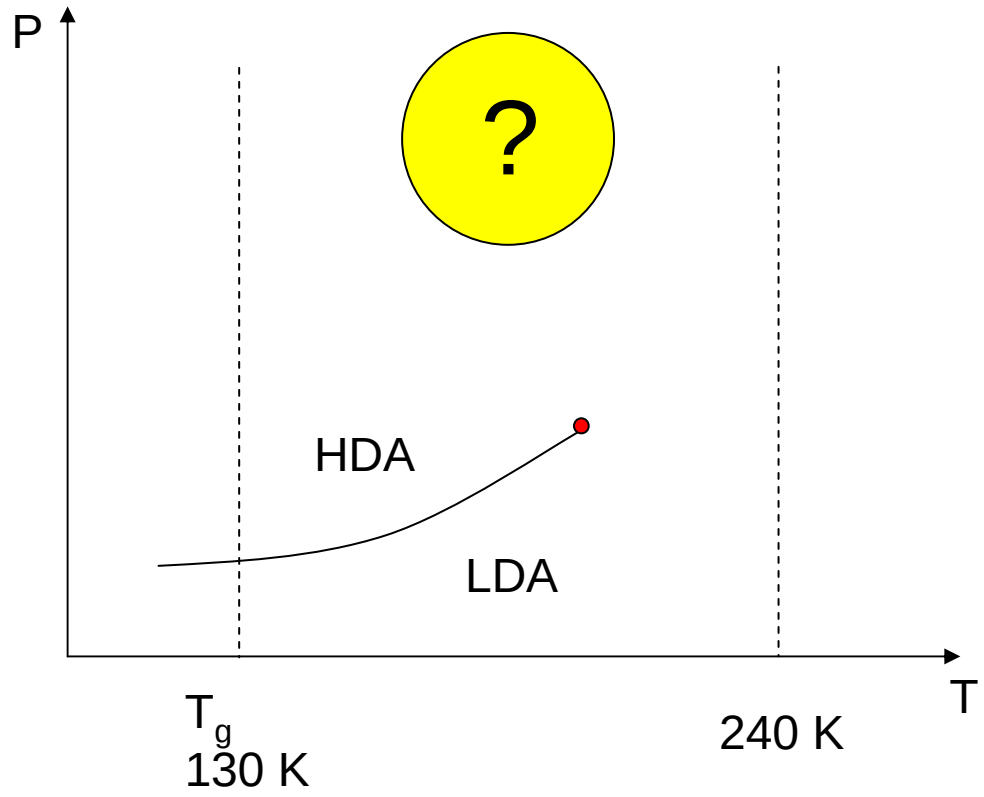
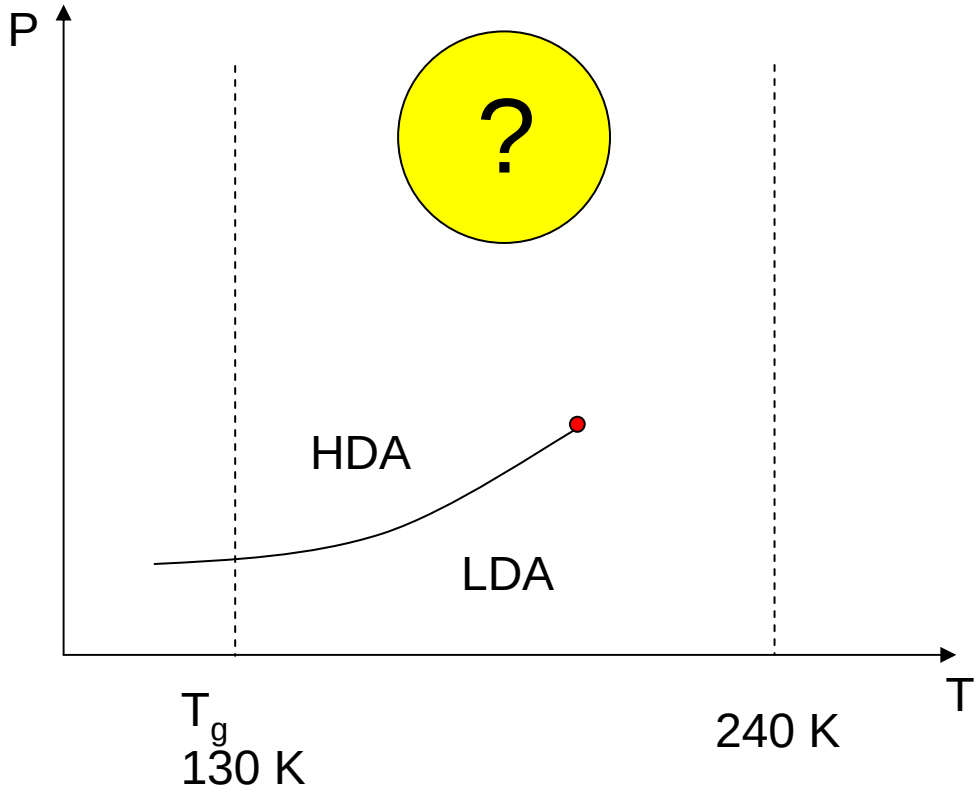
Extrapolation/ Speculation LT Critical point (1998)

Pour la Science ***285***, *84 (2001)*





O. Mishima and H.E. Stanley
*Nature **396**, 329 (1998)*



+

Computer simulations of molecular dynamics using
« effective potentials »

Acronym (date)	Status	Type	Sites	$\mu_g(D)$	$\mu_l(D)$
BF (1933)	empirical	R	4	2.0	2.0
R (1951)	empirical	R	5	1.84	1.84
BNS (1971)	empirical	R	5	2.17	2.17
ST2 (1973,1993)	empirical	R	5	2.35	2.35
CF (1975,1978,1995)	empirical	F	3	1.86	1.98
MCY (1976)	ab initio	R	4	2.19	2.19
DCF (1978,1980,1993)	empirical	F,D,P	3	1.855	-
PE (1979)	empirical	P	1	1.855	2.50
SPC (1981)	empirical	R	3	2.27	2.27
TIP3P (1981,1983)	empirical	R	3	2.35	2.35
RWK (1982)	empirical	F	4	1.85	1.89
TIP4P (1983)	empirical	R	4	2.18	2.18
BJH (1983)	empirical	F	3	1.87	1.99
SPC/F (1985)	empirical	F	3	2.27	2.42
MCYL (1986)	ab initio	F	4	2.19	2.26
SPC/E (1987)	empirical	R	3	2.35	2.35
WK (1989)	empirical	R	4	2.60	2.60
SPCP (1989)	empirical	P	3	1.85	2.90
CKL (1990)	empirical	F,P	4	1.88	2.20
MCHO (1990)	ab initio	P	6	2.12	≈3.0
NCC (1990)	ab initio	P	6	1.85	2.80
NEMO (1990,1995)	ab initio	P	5	2.04	2.89
PTIP4P (1991)	empirical	P	4	1.85	2.80
SPC/FP (1991)	empirical	F,P	3	1.85	2.44
PSRWK (1991)	empirical	P	4	1.88	2.63
KJ (1992)	empirical	P	4	1.85	-
NCCvib (1992)	ab initio	F,P	6	1.85	3.11
ASP-W (1992,1998)	ab initio	P	3	1.85	2.90
RPOL (1992)	empirical	P	3	2.02	2.62
CPMD (1993,1999)	DFT+CP	F,D,P	nucl.+el.	1.87	2.95
PPC (1994)	ab initio	P	4	2.14	2.51
SPC/FQ (1994)	empirical	P	3	1.85	2.83
TIP4P/FQ (1994)	empirical	P	4	1.85	2.62
KKY (1994)	empirical	F,D	3	2.38	2.21
SQPM (1995)	valence bond	P	4	1.85	2.62
SCPDP (1996)	empirical	P	4	1.85	2.87
TAB/10D (1998)	SCF+MD	P	5	1.85	2.65
NSPCE (1998)	empirical	R	3	2.18	2.18
NCF (1998)	empirical	F	3	1.85	1.90
MCDHO (2000)	ab initio	F, P	4	1.85	3.01
TIP5P (2000)	empirical	R	5	2.29	2.29
SPC/HW (2001)	empirical	R	3	2.41	2.41
DEC (2001)	empirical	R	3	1.85	1.85
SWFLEX (2001)	empirical	P	4	1.85	2.59
POLARFLEX (2001,2003)	valence bond	F,P	3	1.85	2.55,2.59
POL5 (2001)	ab initio	P	5	1.85	2.71
TTM2/R,F (2002,2006))	ab initio	R(F),P	4	1.85	2.67
SPC/S (2002)	empirical	R	3	2.30	2.30
COS/B2(2002)	empirical	P	3	2.07	2.62
AMOEBA(2003)	empirical	F,P	3	1.77	2.78
SWM4-DP (2003)	empirical	P	4	1.85	2.46
TIP5P/E (2004)	empirical	R	5	2.29	2.29
ABEEM-7P (2004)	empirical	F,P	7	1.85	2.80
COS/G2,G3 (2004)	empirical	P	4	1.85	2.59
TIP3P-PME (2004)	empirical	R	3	2.34	2.34
VRT(ASP-W)III (2005)	ab initio+VRT	F,P	3	1.85	-
GCPM (2005)	empirical	P	4	1.85	2.72
TIP4P/Ew,2005,Ice (2005)	empirical	R	4	2.321, 2.305, 2.426	
QMFF (2006)	ab initio	F,P	6	1.87	-

Bertrand Guillot
2006

Good thermal properties → « Excess » of structure

Good structure → Less « anomalies »

Parameters optimized for room temperature liquid water
Quantum effects not always taken into account
...

Main problem:

Simulations	Real water
Point charges	Spherical molecule
Spherical (electrostatic) potentials	Anisotropic potential
	↓
	Hydrogen bonds

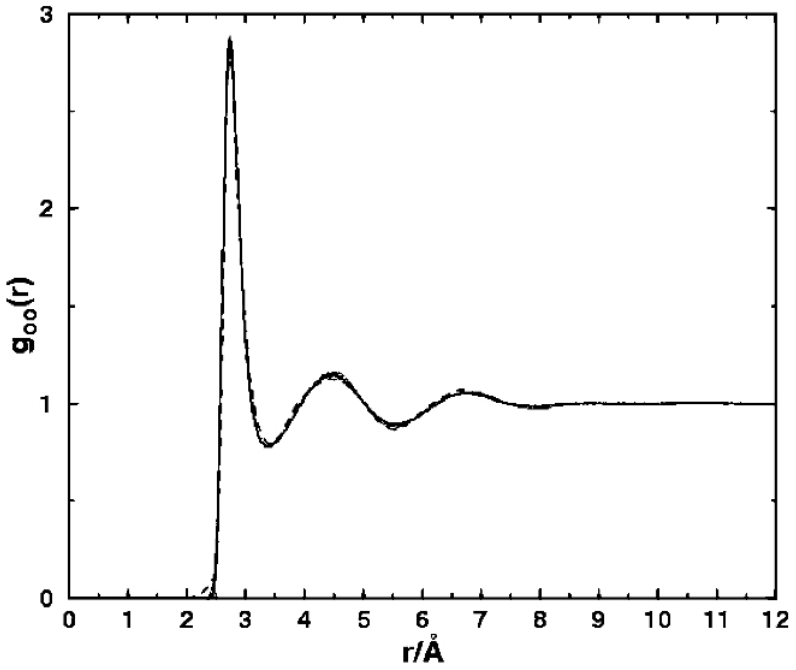
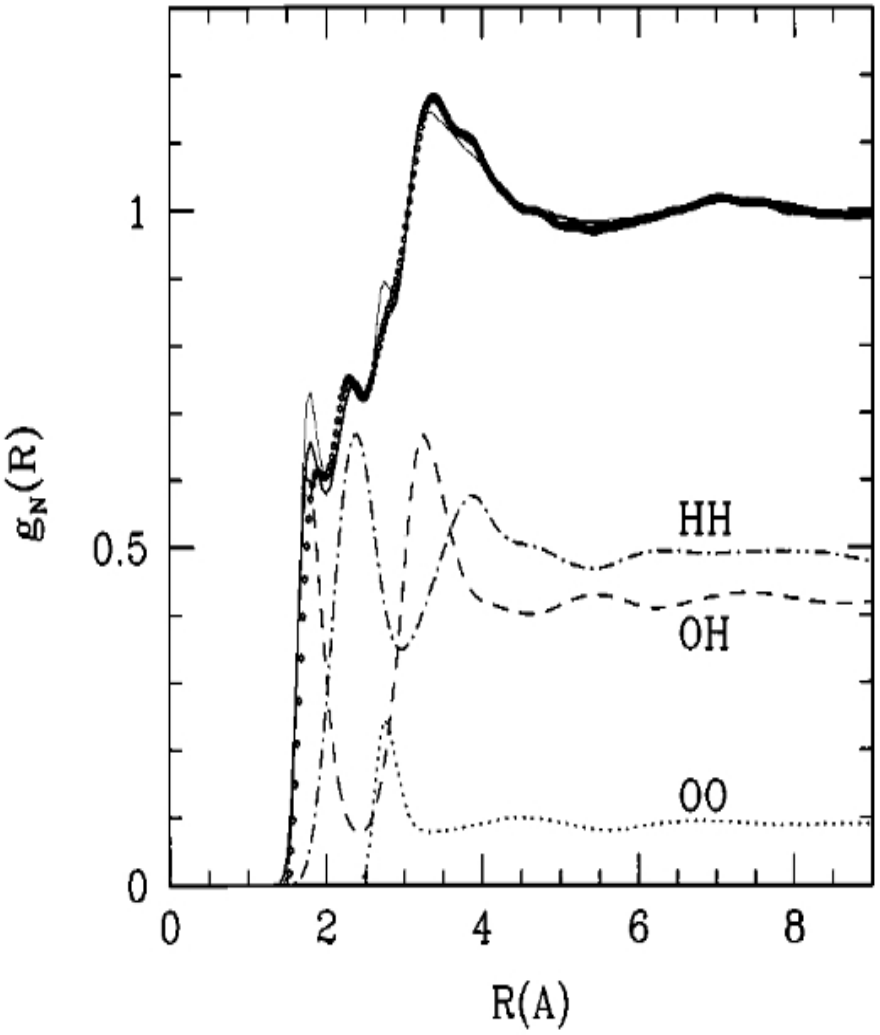
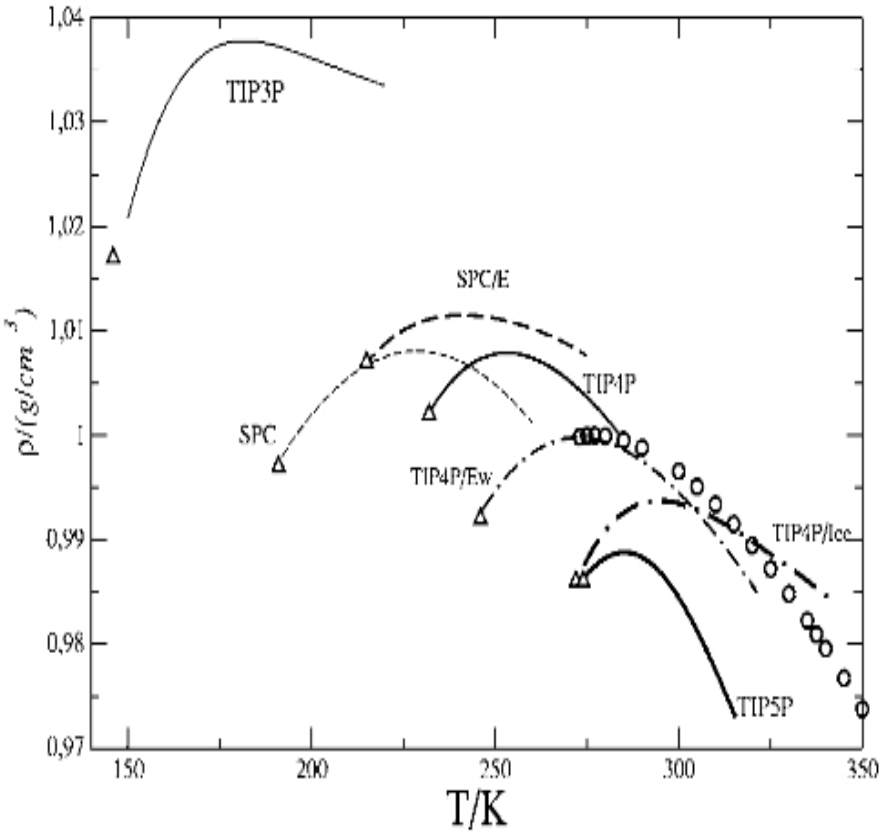


Fig. 1 Comparison of $g_{OO}(r)$ derived from r-space fitting using ALS experimental data[2] (dashed line) and neutron experimental data and empirical potential structural refinement (black line).[14]

RX: Hura et al. (2000), JCP 113,9140
Neutrons: Soper (2000), Chem. Phys. 258, 121



Simulation: Guillot and Guissani (2001), JCP 114, 6720
Exp.: Bellissent-Funel et al. (1997), JCP 107, 2942



*Vega et al. (2005), JCP **123**, 144504*

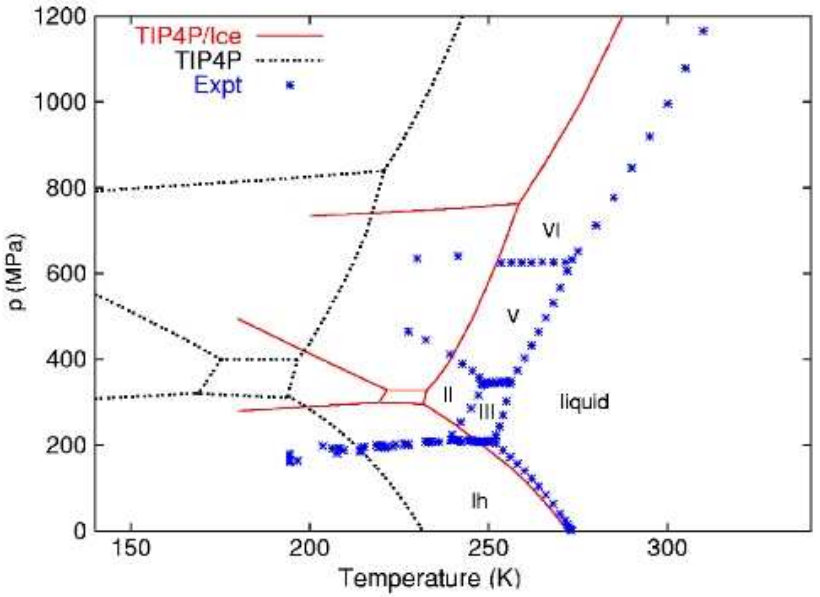


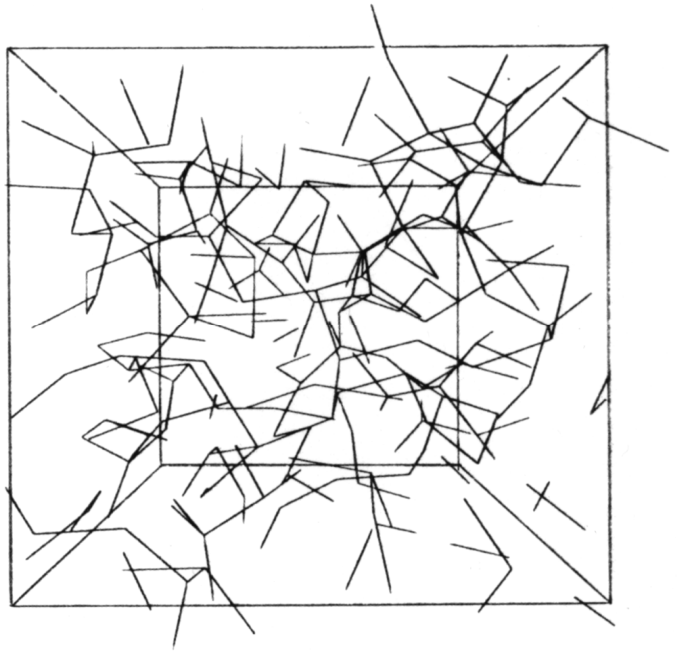
FIG. 1. The phase diagram of TIP4P/Ice (full lines) and TIP4P (dashed) compared to the experiment (stars). The labels mark the domain of stability of the ice phases in the experimental phase diagram.

*Abascal et al. (2005), JCP **122**, 234511*

- Large number of hydrogen bonds

- Local tetrahedral symmetry

- Short life time of the bonds



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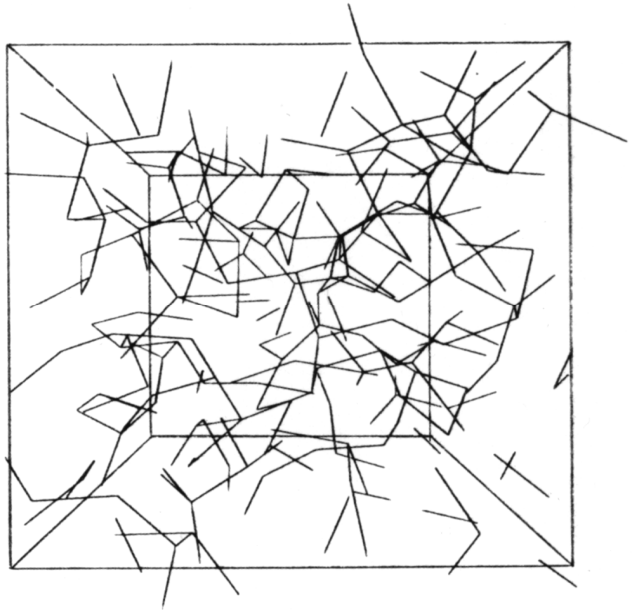
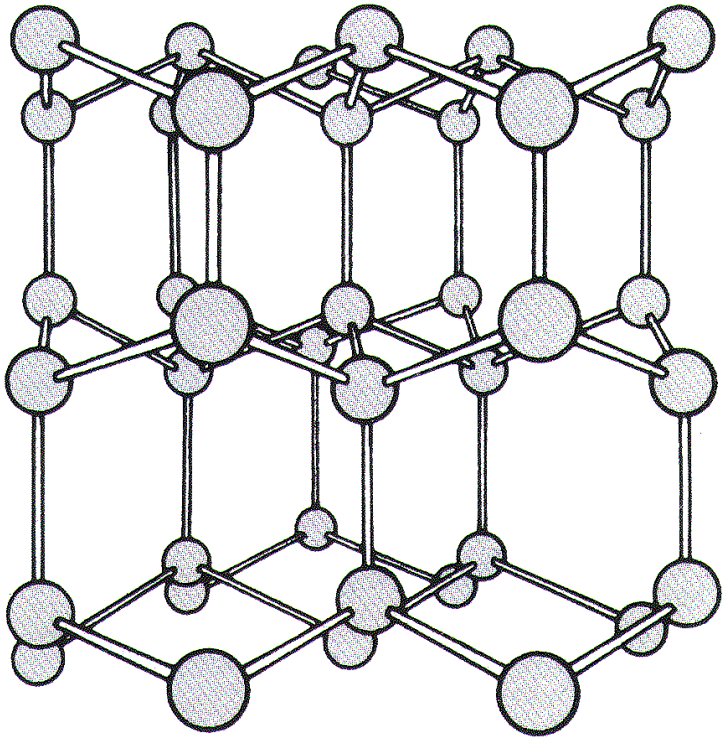
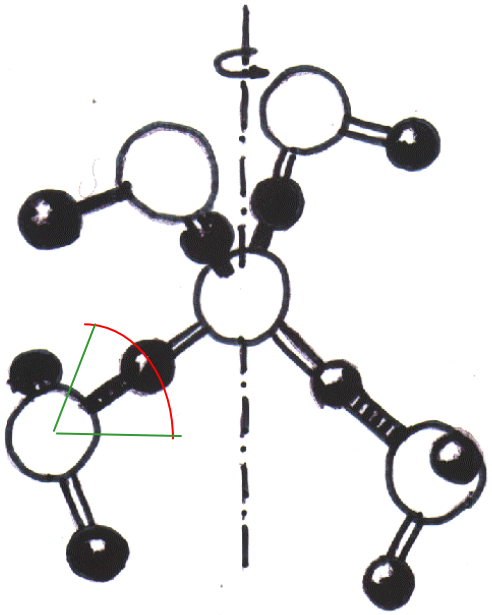


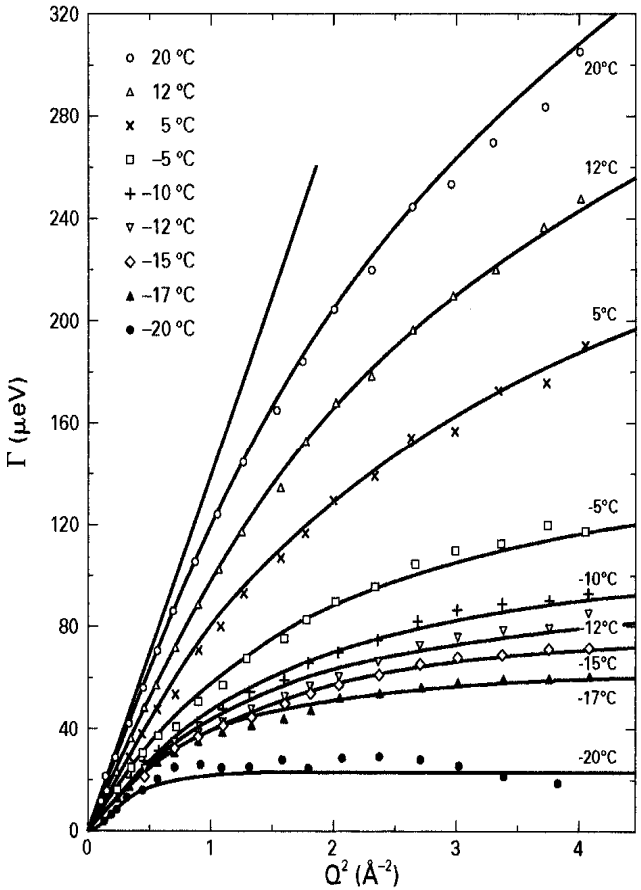
How to tackle HB dynamics?

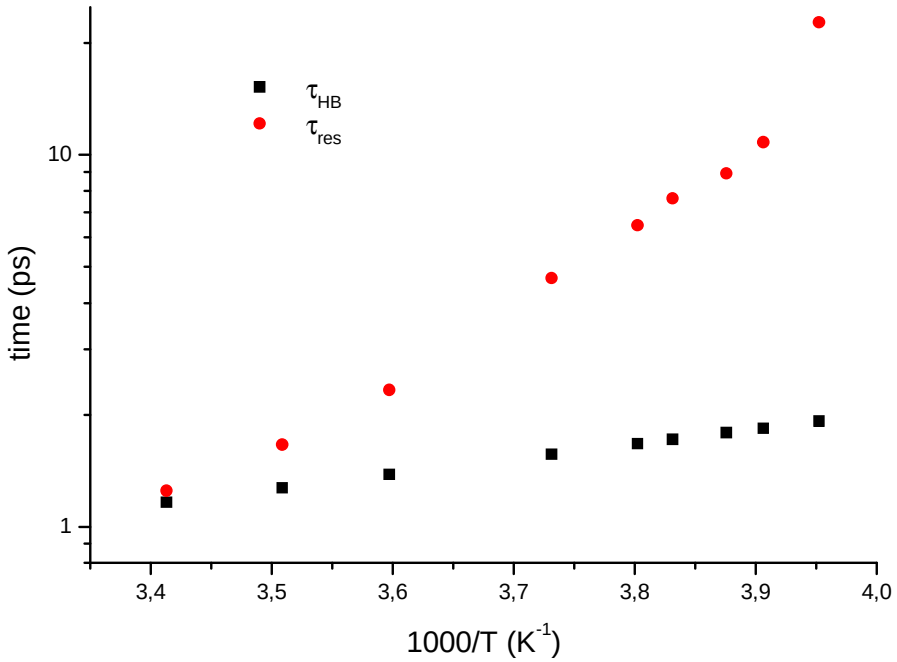
Librations and HB dynamics





HB and residence times (QENS)





J. Teixeira, M.-C. Bellissent-Funel, S.-H. Chen and A.J. Dianoux
Phys. Rev. ***A31****, 1913 (1985)*

Bulk and confined water

$$\tau_{HB} / ps = 0.0485 \exp(931/T)$$

$$E_{HB} = 1.85 kcal/mol$$

$$p_B = n_{HB}/4 = 1.8 - 0.004T$$

Bulk

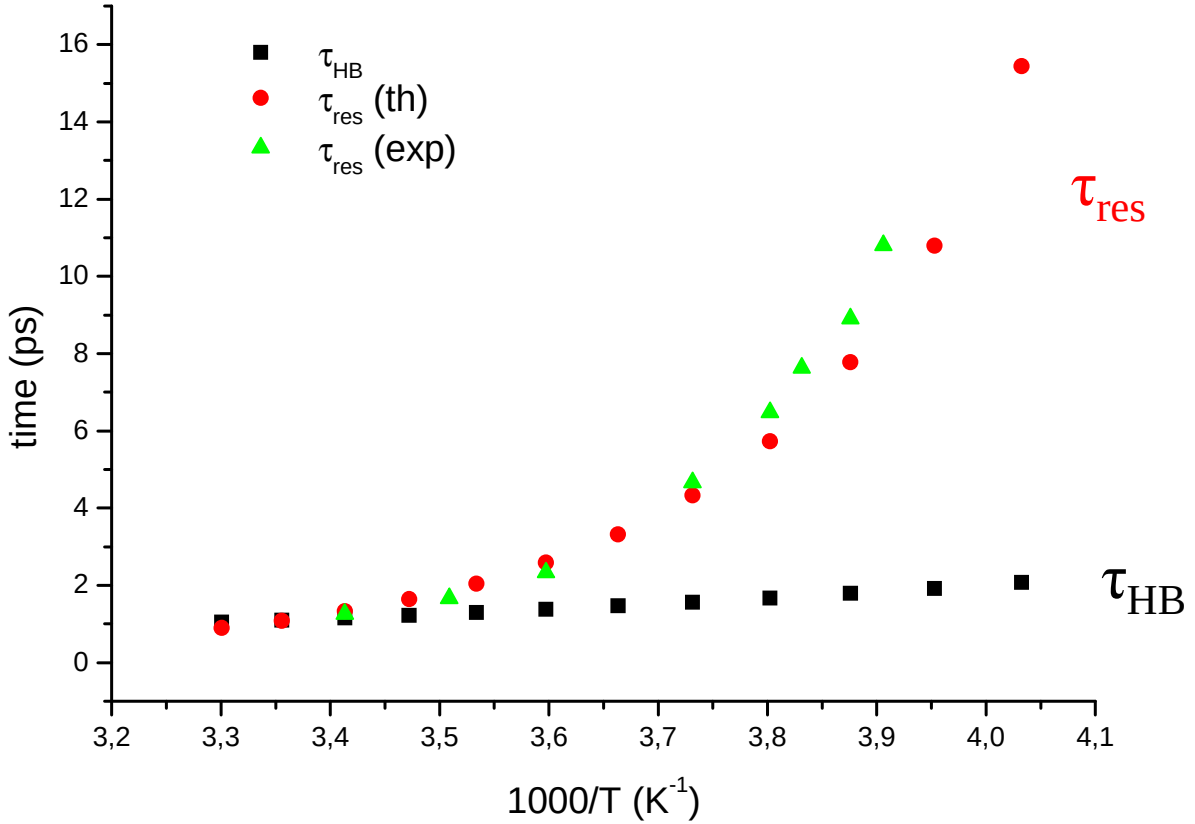
$$F_I^4 = 6p_B^2 - 8p_B^3 + 3p_B^4$$

$$\tau_{res}^{bulk} = const\left(\frac{\tau_{HB}}{-\ln\left(F_I^4\right)}\right)$$

Confined

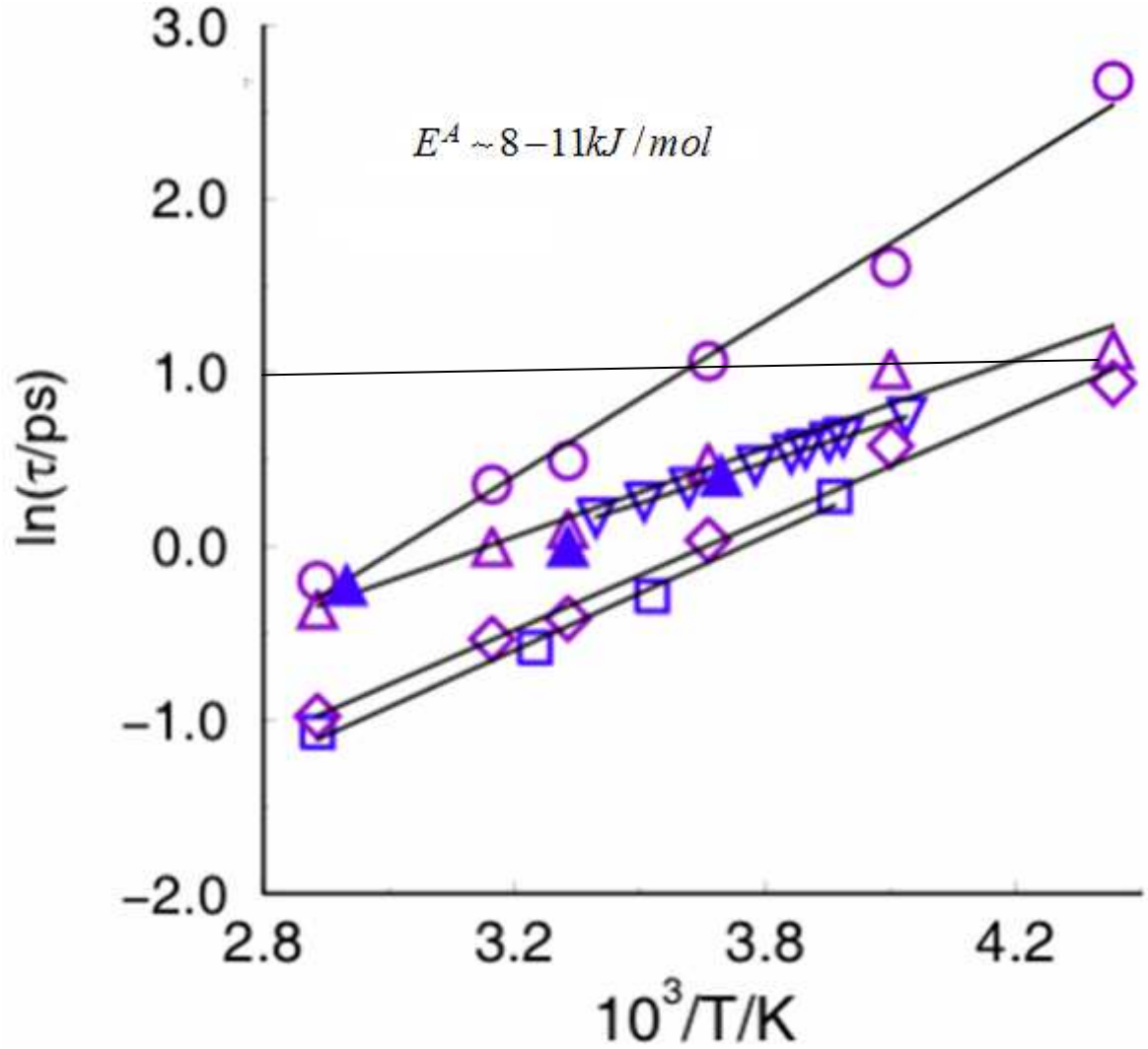
$$F_I^3 = 3p_B - 3p_B^2 + p_B^3$$

$$\tau_{res}^{conf} = const\left(\frac{\tau_{HB}}{-\ln\left(F_I^3\right)}\right)$$


τHB
τres (th)
τres (exp)
τres
τHB
time (ps)
1000/T (K-1)
0
2
4
6
8
10
12
14
16
3,2
3,3
3,4
3,5
3,6
3,7
3,8
3,9
4,0
4,1

Microscopic measurements of the dynamics of H bonds show there are NO anomalies at their level

*J. Teixeira, A. Luzar and S. Longeville, J. Phys.: Cond. Matter **18**, S2353 (2006)*



DepLS

QENS

J.T. *et al* **1984,1985,2002**

IR hole burning- Laubereau 1998,2001

Molecular dynamics

***1/k* = HB lifetime**

***1/k'* = HB reforming time**

***1/(k+k')* = time for switching H bond partners**

Microscopic measurements of the dynamics of H bonds show there are NO anomalies at their level

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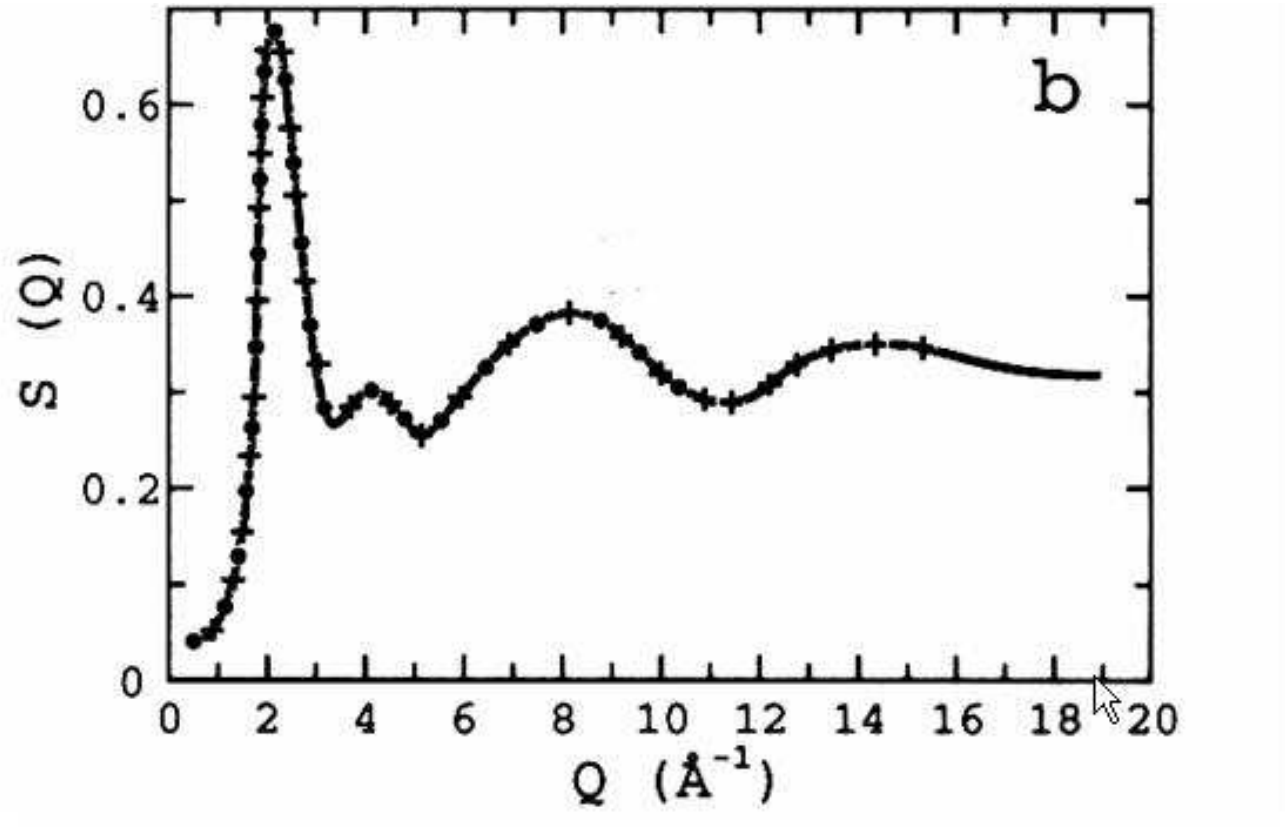
*J. Phys.: Cond. Matter **18**, S2353 (2006)*

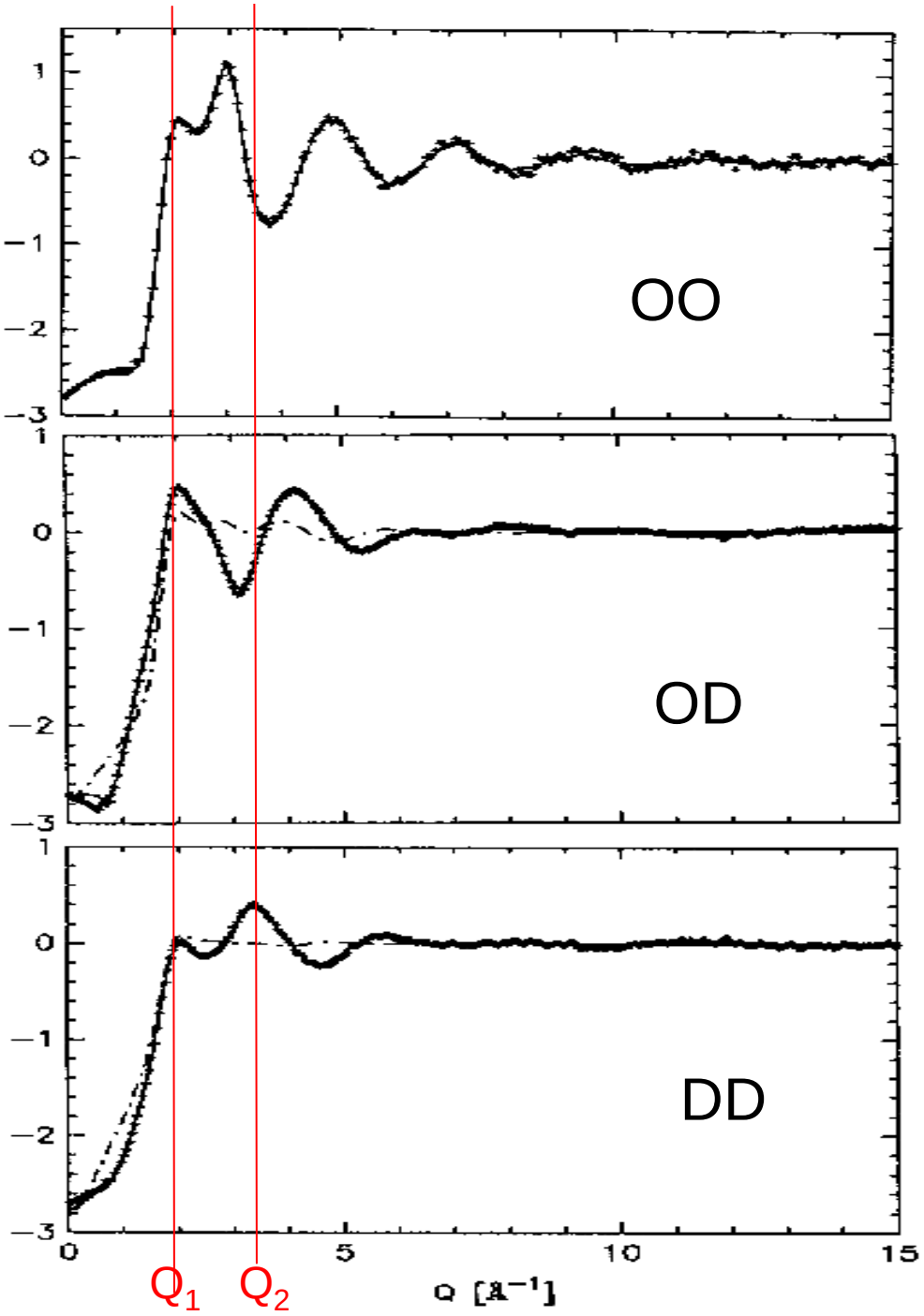
Structure factor of liquid water (neutrons)



S(Q) partials

A.K. Soper in Hydrogen Bond Networks ed. M.-C. Bellissent-Funel and J. Dore (Kluwer, Dordrecht, 1994), p. 97

$Q_1 = 1.9$ Å^{-1}
$Q_2 = 3.7$ Å^{-1}



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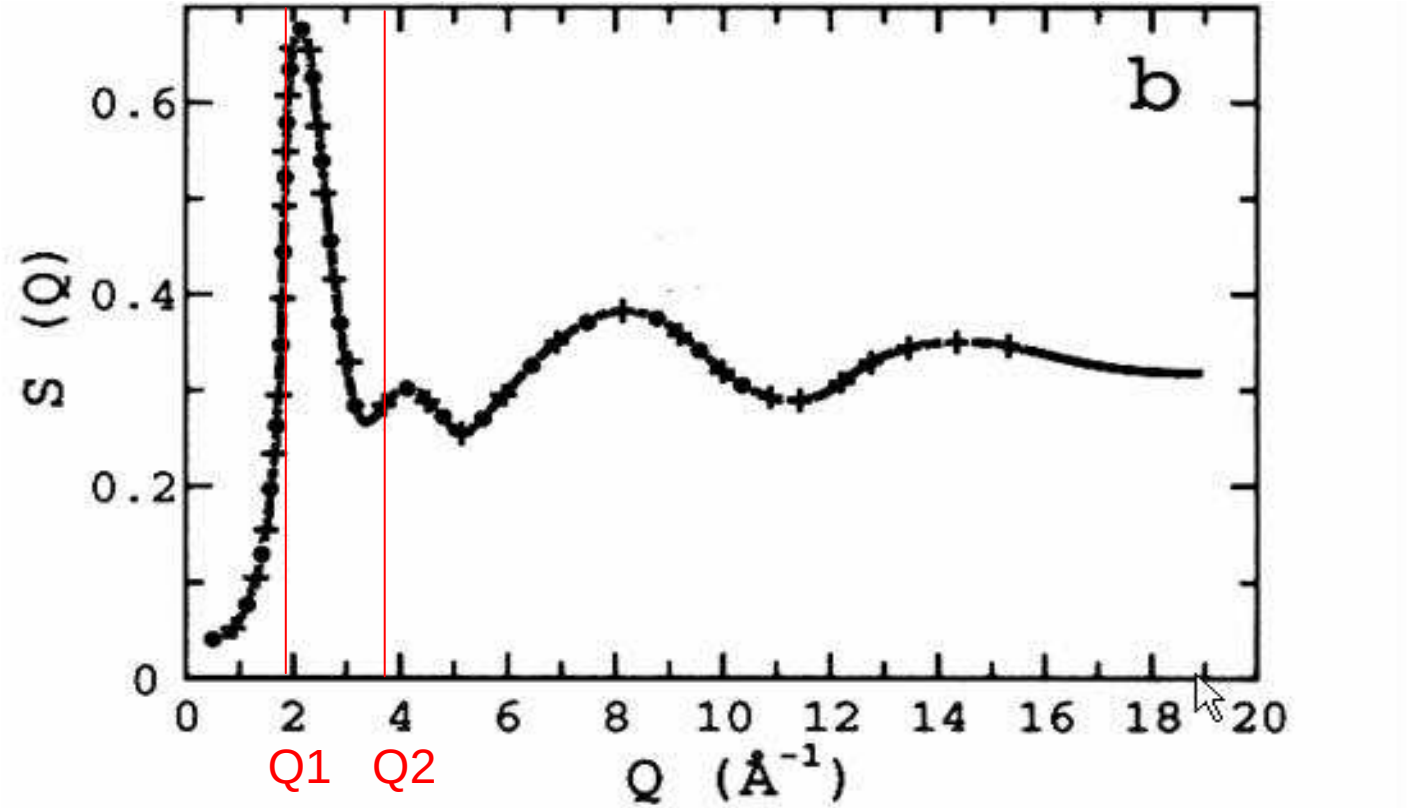
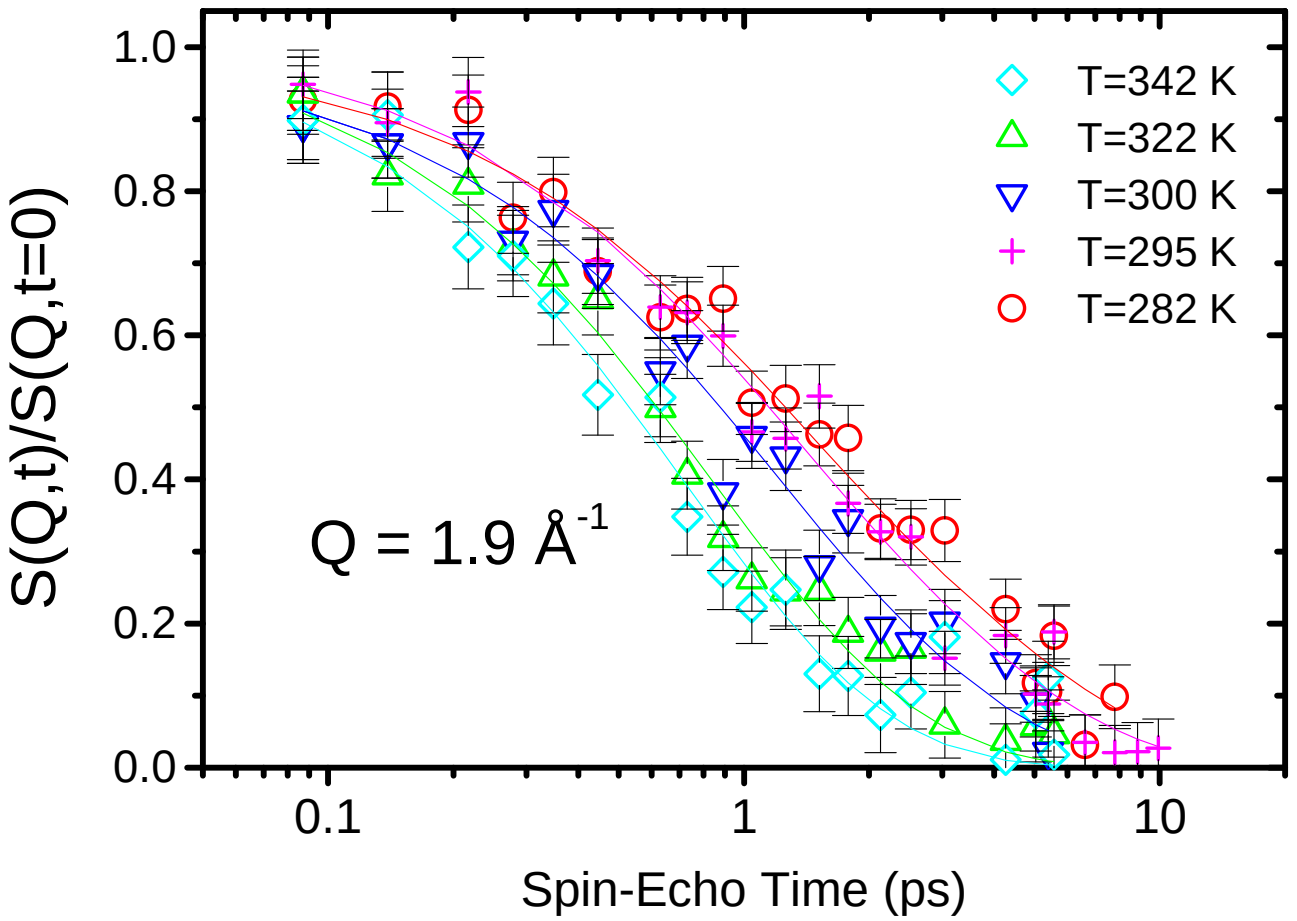
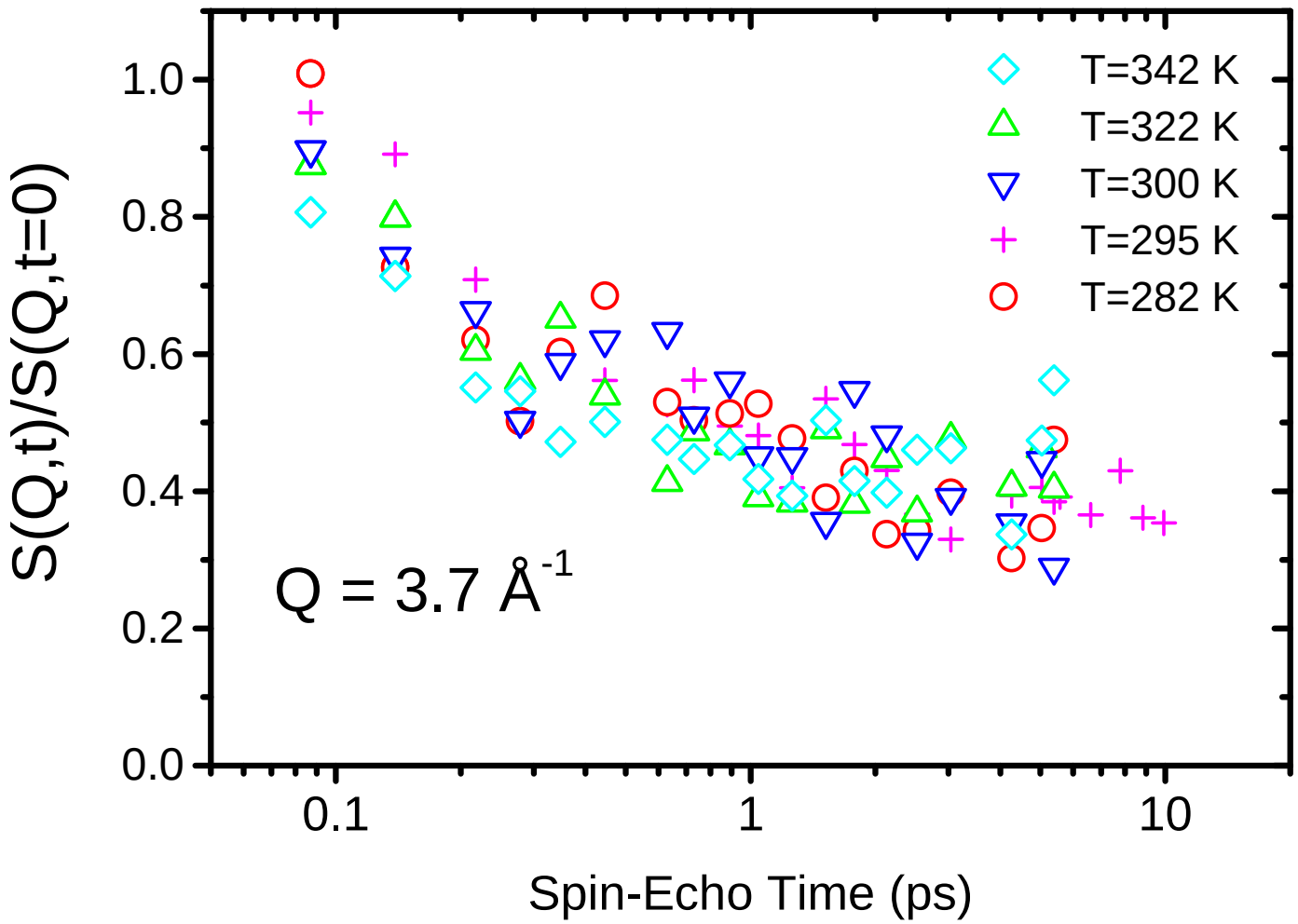
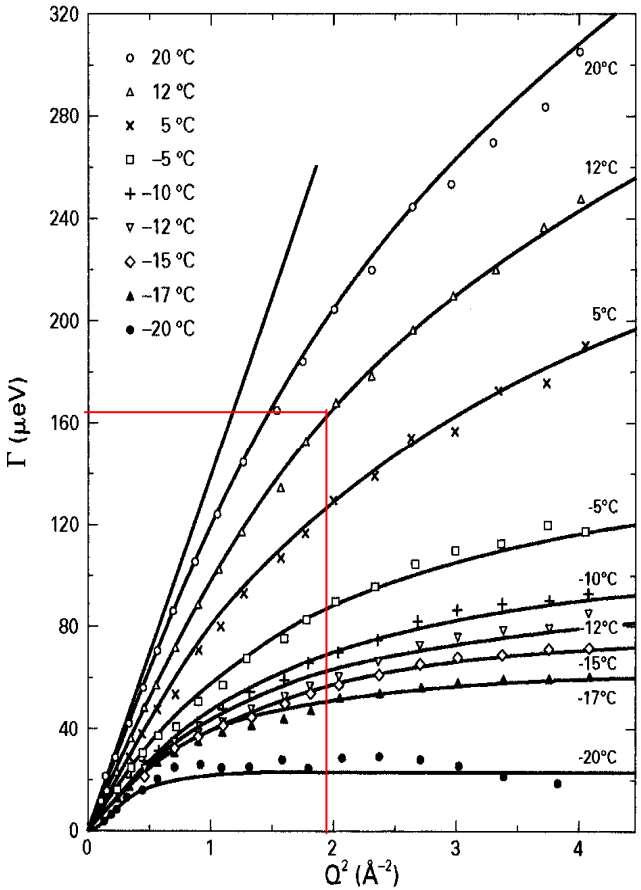


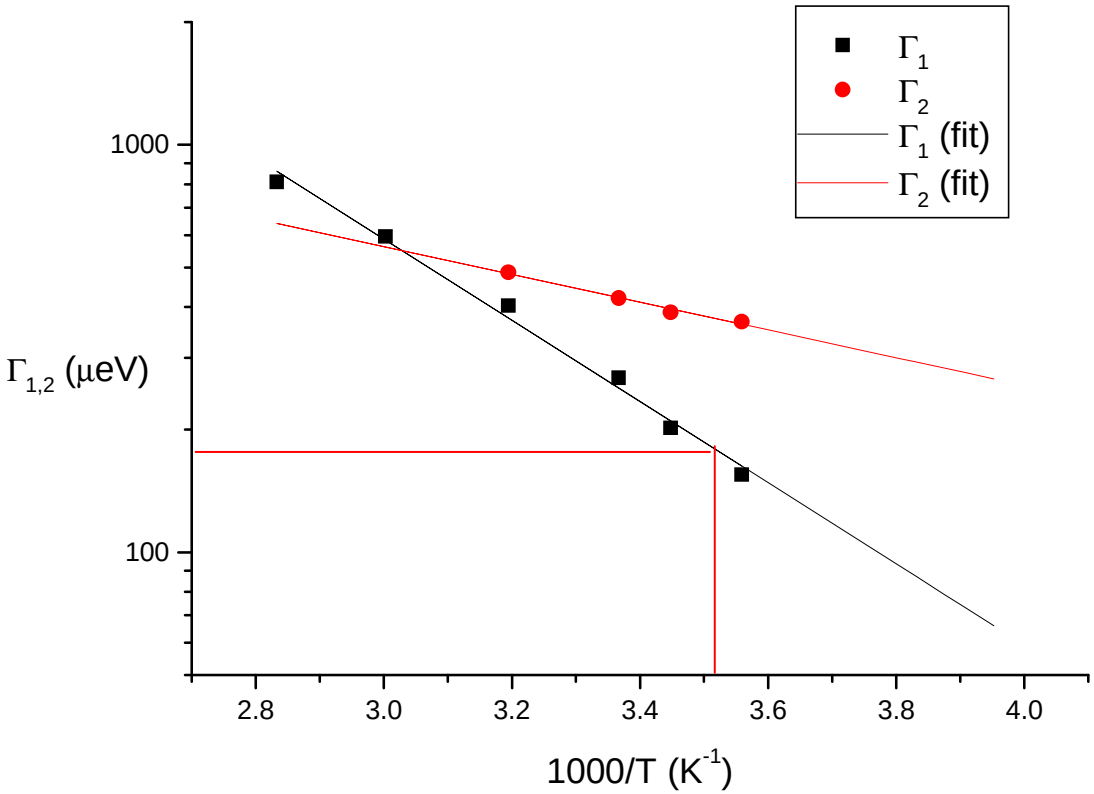
Intermediate scattering function



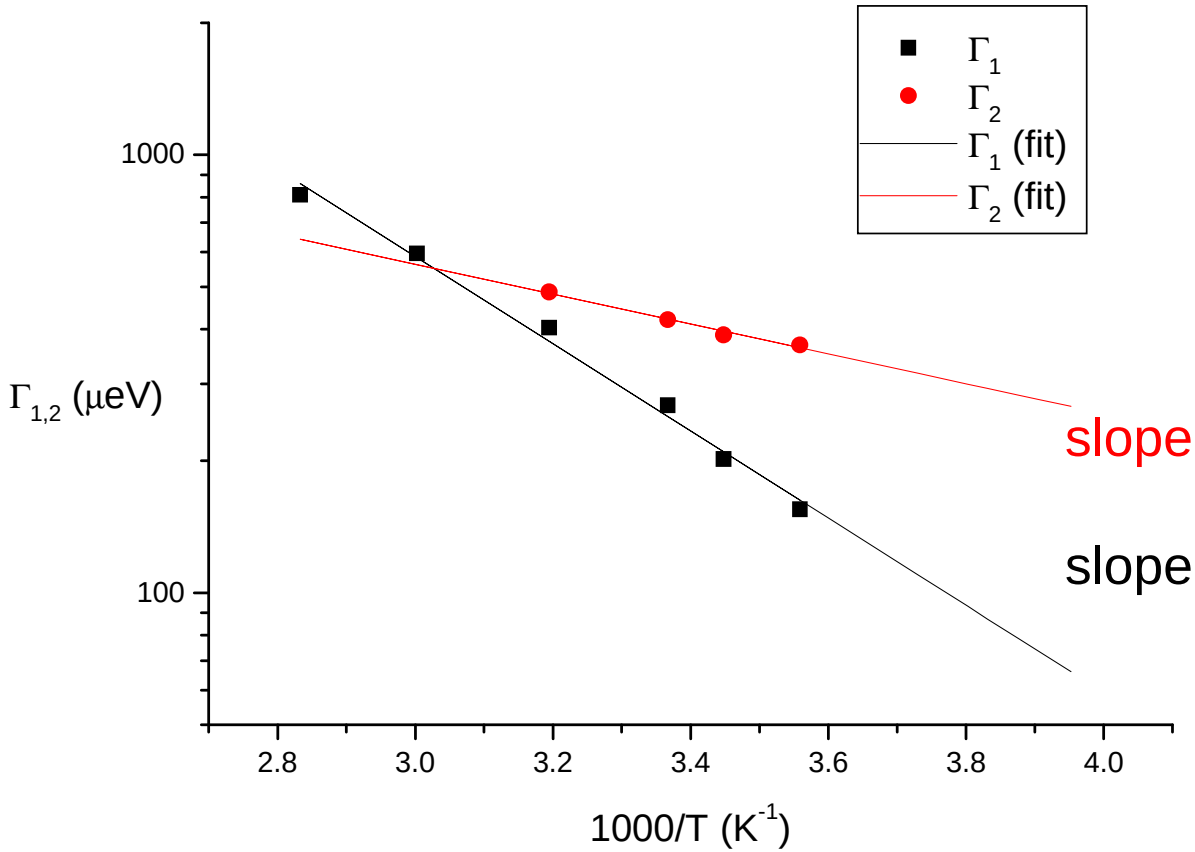
Intermediate scattering function




20 °C
12 °C
5 °C
−5 °C
−10 °C
−12 °C
−15 °C
−17 °C
−20 °C
20°C
12°C
5°C
-5°C
-10°C
-12°C
-15°C
-17°C
-20°C
Γ (μeV)
Q² (Å⁻²)


Γ1
Γ2
Γ1 (fit)
Γ2 (fit)
Γ1,2 (μeV)
1000/T (K-1)

Line widths



slope: 1.85 kcal/mol

slope: 4.56 kcal/mol

$$\frac{4.56}{1.85} = 2.46 = n_{HB} \qquad p_{HB} = n_{HB} / 4 = 0.615 \qquad T = 296K = 23°C$$

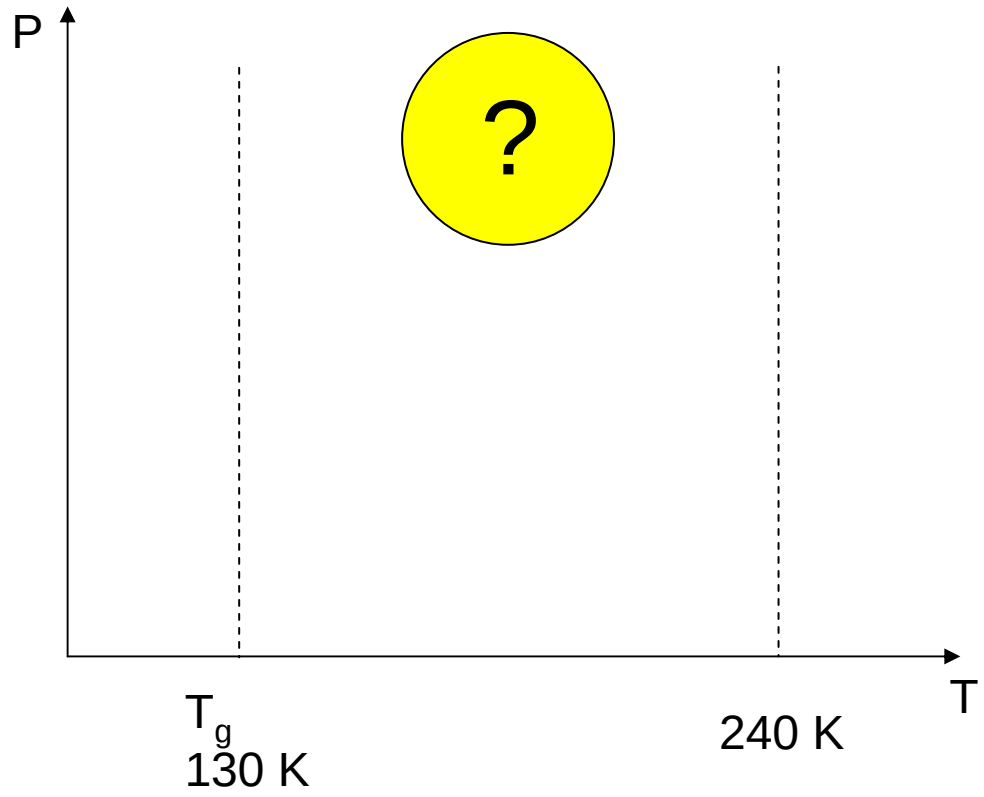
Experimental features

There is no discontinuity or divergence of any property of liquid water

Several independent experiments show that:

Hydrogen bond dynamics has an Arrhenius temperature dependence

It is possible to evaluate a "molecular time“
from the HB dynamics and from the number of intermolecular bonds.
Its temperature dependence is strongly non-Arrhenius


P
?
T
T_g
130 K
240 K

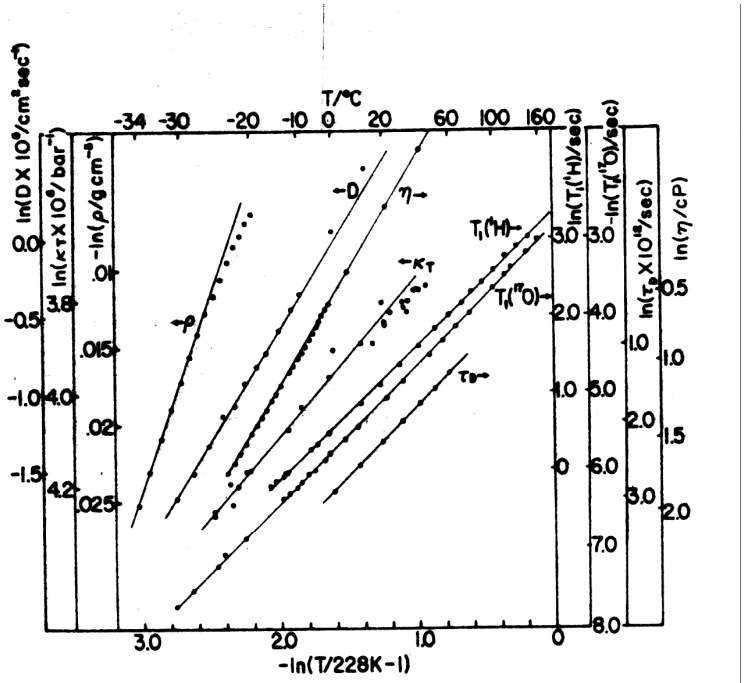


FIG. 4. $\ln W$ vs $\ln(T/T_s - 1)$ for the physical properties X of water at atmospheric pressure. The plots illustrate the applicability of Eq. (3) in the lowest temperature range for which data are available for each property. The temperature T_s = 228 K is used in each case although fractionally improved least squares best fits can be obtained with T_s up to 7 °C removed from 228 K in individual cases. Data: ρ (density), (11,12) D (diffusion coefficient),[15] η (viscosity),[16] κ_T (isothermal compressibility), T_1 (^{1}H) (proton spin lattice relaxation time),[17] T_1 (^{17}O) (oxygen spin lattice relaxation time)[18] τ_D (dielectric relaxation time).[19]

R. Speedy and C.A. Angell
J. Chem. Phys. **65**, *851 (1976)*

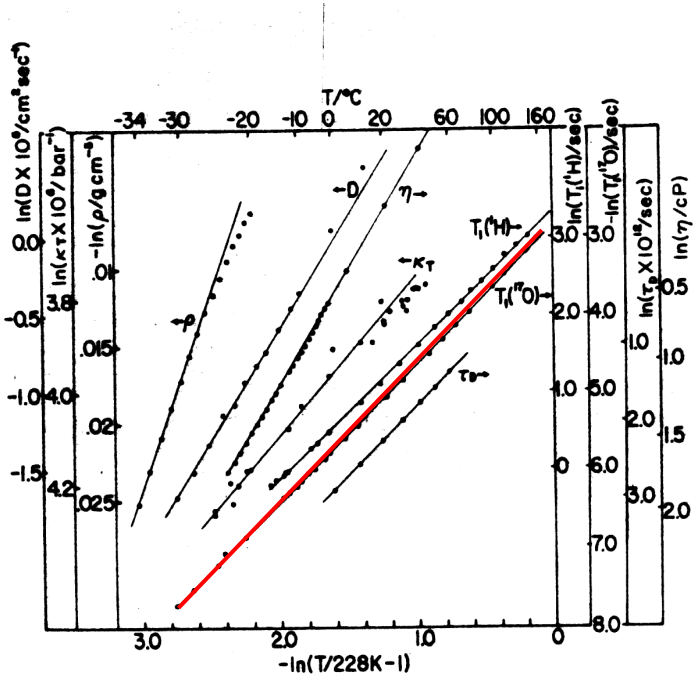
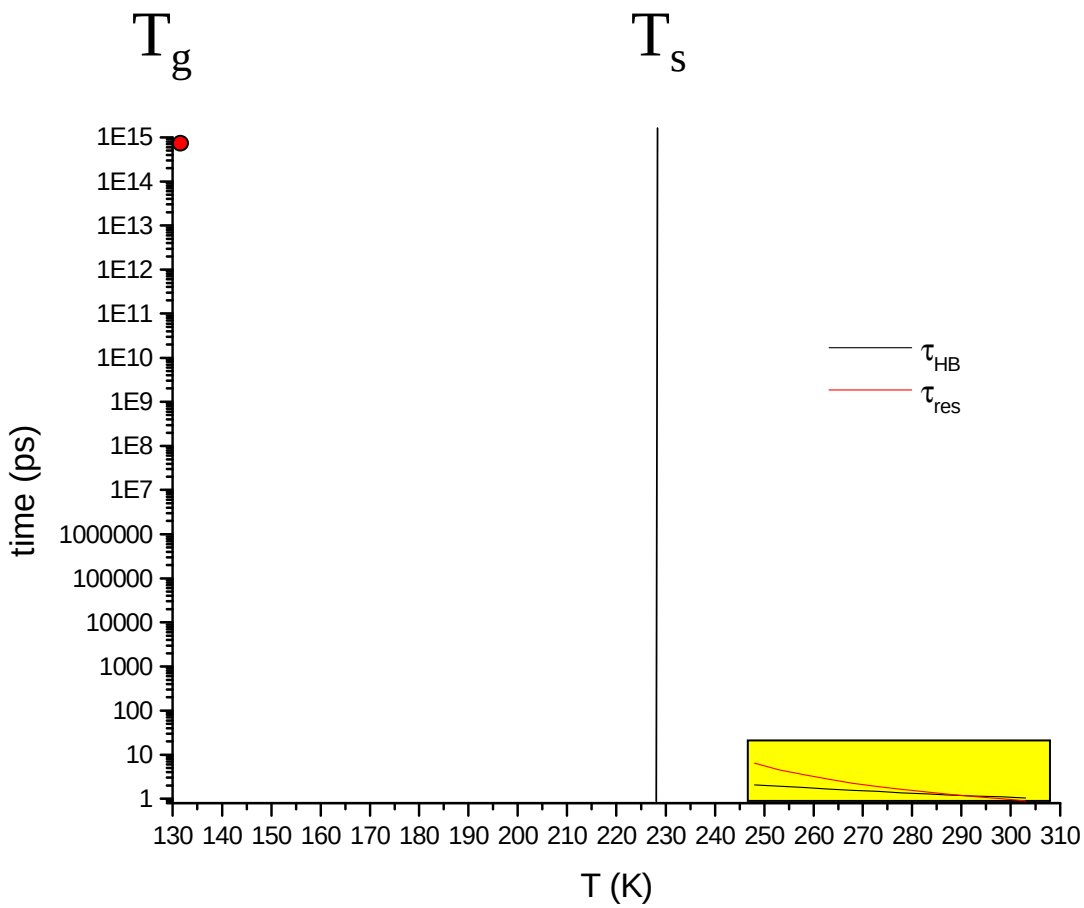


FIG. 4. ln$W$ vs ln$(T/T_s - 1)$ for the physical properties X of water at atmospheric pressure. The plots illustrate the applicability of Eq. (3) in the lowest temperature range for which data are available for each property. The temperature T_s = 228 K is used in each case although fractionally improved least squares best fits can be obtained with T_s up to 7 °C removed from 228 K in individual cases. Data: ρ (density), (11,12) D (diffusion coefficient),[15] η (viscosity),[16] κ_T (isothermal compressibility), T_1 (^{1}H) (proton spin lattice relaxation time),[17] T_1 (^{17}O) (oxygen spin lattice relaxation time)[18] τ_D (dielectric relaxation time).[19]



R. Speedy and C.A. Angell
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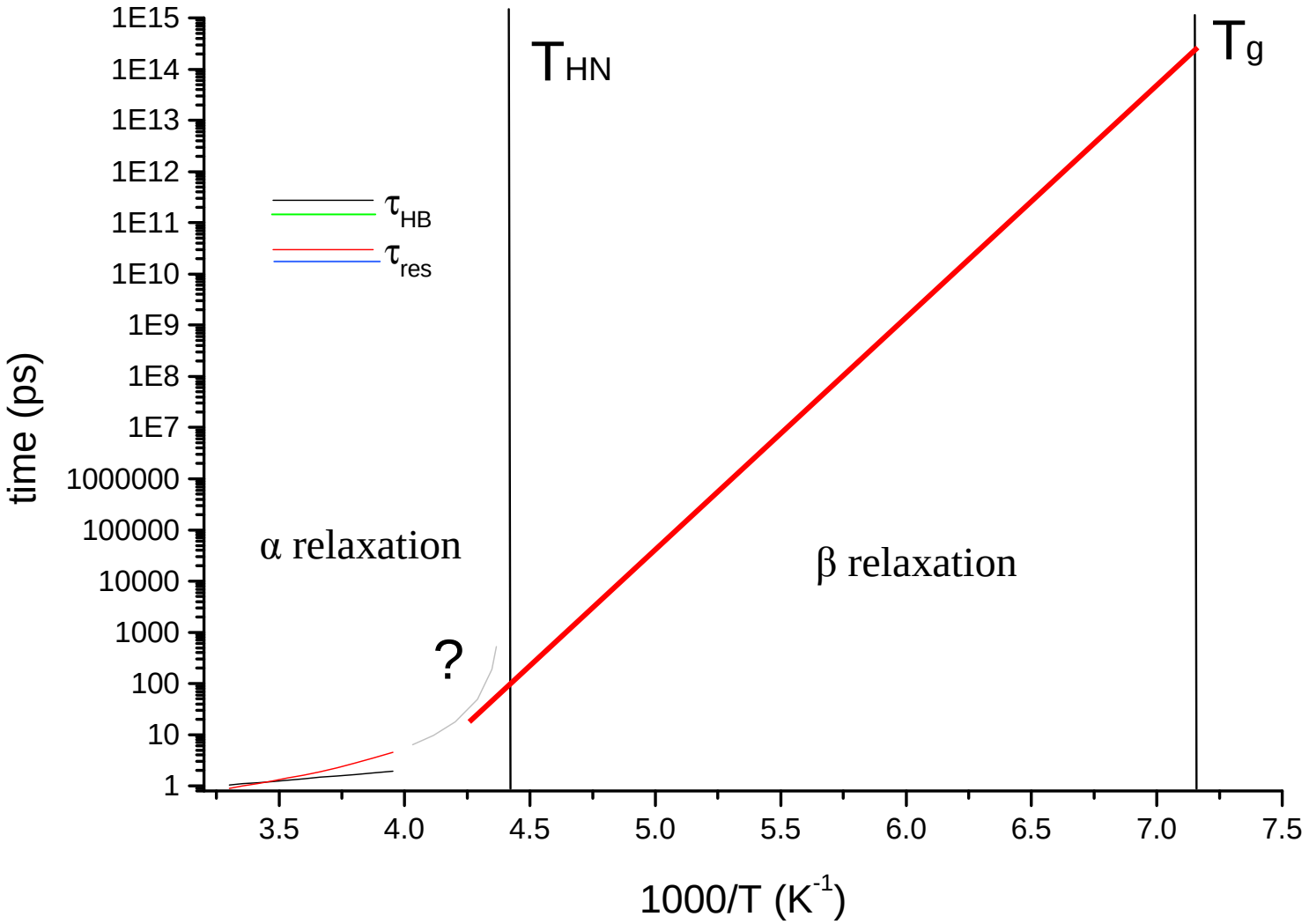
A transition to Arrhenius temperature dependence?



Conclusions

1) There are two main characteristic times :

a) A molecular residence time, τ_{res}, with a strong non-Arrhenius temperature dependence.
It shows an apparent divergence at the temperature of the homogeneous nucleation of hexagonal ice (-45 °C)

b) The hydrogen bond characteristic time, τ_{HB}, with an Arrhenius temperature dependence

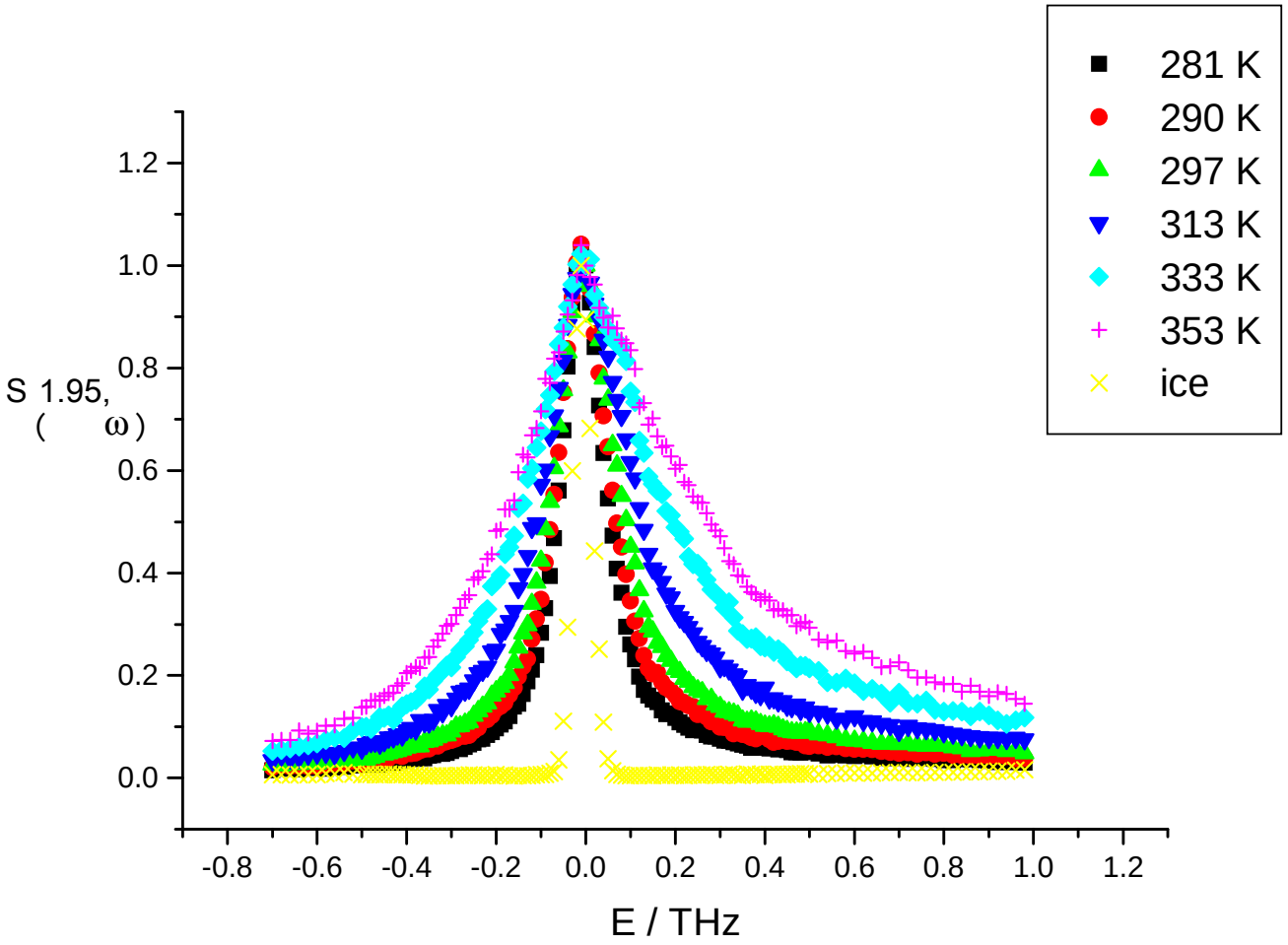
2) The anomalous temperature dependence of τ_{res}
can be predicted from τ_{HB} and the tetrahedral network of hydrogen bonds

3) During the quenching of bulk liquid water, if ice nucleation is avoided,
there is a transition from a non-Arrhenius molecular behaviour to
the Arrhenius temperature dependence of hydrogen bond dynamics.
It can be seen like a fragile to strong transition taking place at the homogeneous nucleation temperature, T_H.

4) In some confined media, if the nucleation of ice cannot take place,
a similar transition is observed around 200 K

$S(Q,\omega)$ (D_2O)

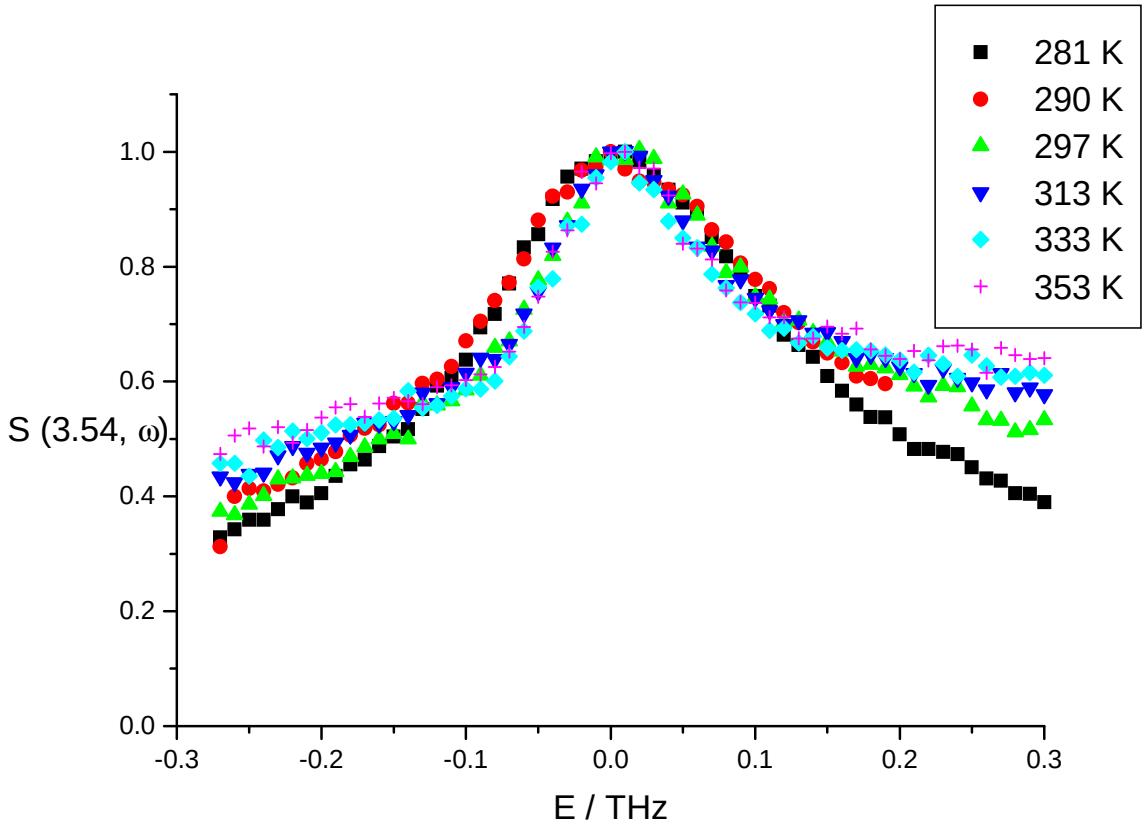
$Q = 1.95$ Å^{-1}

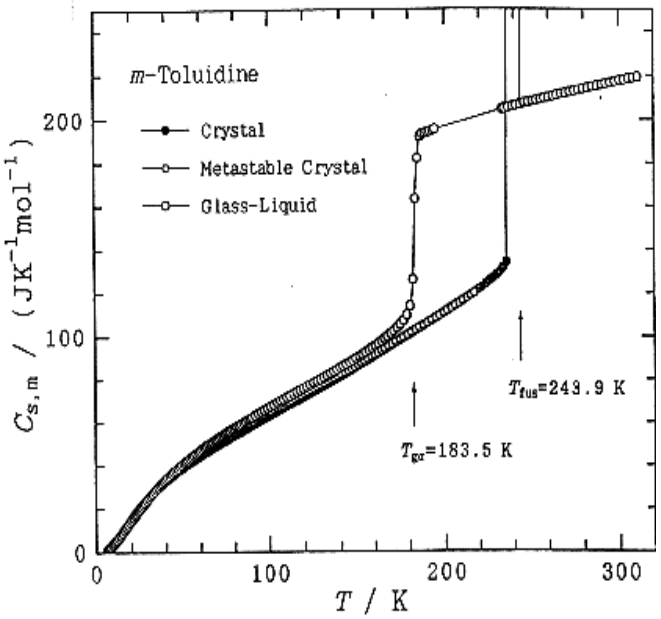


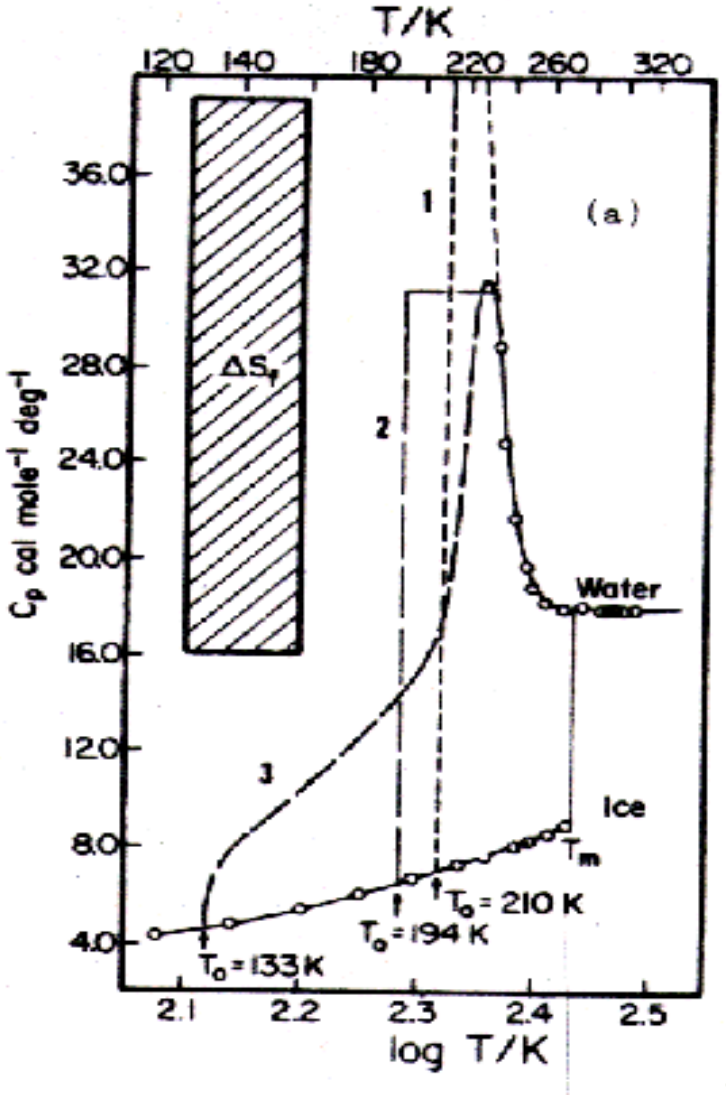
$S(Q,\omega)$ (D_2O)

$Q = 3.54$ Å^{-1}

DD




m-Toluidine
Crystal
Metastable Crystal
Glass-Liquid
$C_{s,m}$ / ($JK^{-1}mol^{-1}$)
T_{fus}=243.9 K
T_{gs}=183.5 K
T / K


T/K
C_p cal $mole^{-1}$ deg^{-1}
ΔS_f
(a)
Water
Ice
T_m
T_0 = 210 K
T_0 = 194 K
T_0 = 133 K
log T/K

H_2O:

$$S(Q) = (13.0\ S^{s}_{HH} + 0.34\ S^{s}_{OO}\ )$$

$$+ (0.56\ S^{d}_{HH} - 0.87\ S^{d}_{OH} + 0.34\ S^{d}_{OO})$$

D_2O:

$$S(Q) = (1.22\ S^{s}_{DD} + 0.34\ S^{s}_{OO}\ )$$

$$+ (1.78\ S^{d}_{DD} + 1.55\ S^{d}_{OD} + 0.34\ S^{d}_{OO})$$