Amorphous Ices
Part 2: Dynamics

Thomas Loerting
Institute of Physical Chemistry
University of Innsbruck

Erice, Sicily
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"Water and Water Systems: 3rd course on "Neutron Science and Instrumentation"

Collaboration

Karsten Köster, Agnes Raidt, Helge Nelson,
Catalin Gainaru, Roland Böhmer

technische universität dortmund

Florian Löw, Carolin Wittich, Franz Fujara

TECHNISCHE UNIVERSITÄT DARMSTADT

Burkhard Geil

GEORG-AUGUST-UNIVERSITÄT GÖTTINGEN

Nicolas Giovambattista

Brooklyn College The City University of New York

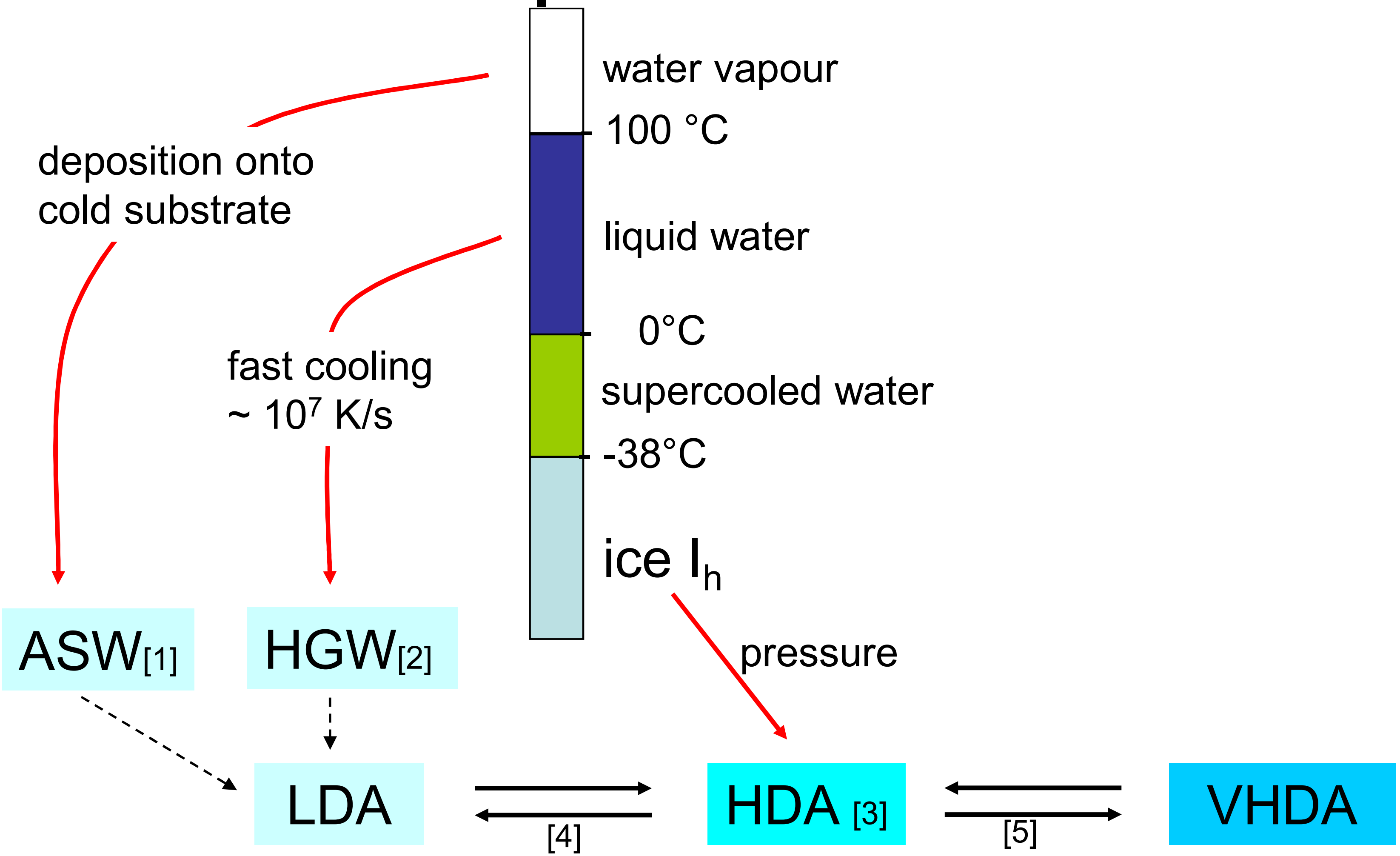
Boris R. Lukanov, Francis W. Starr

WESLEYAN UNIVERSITY

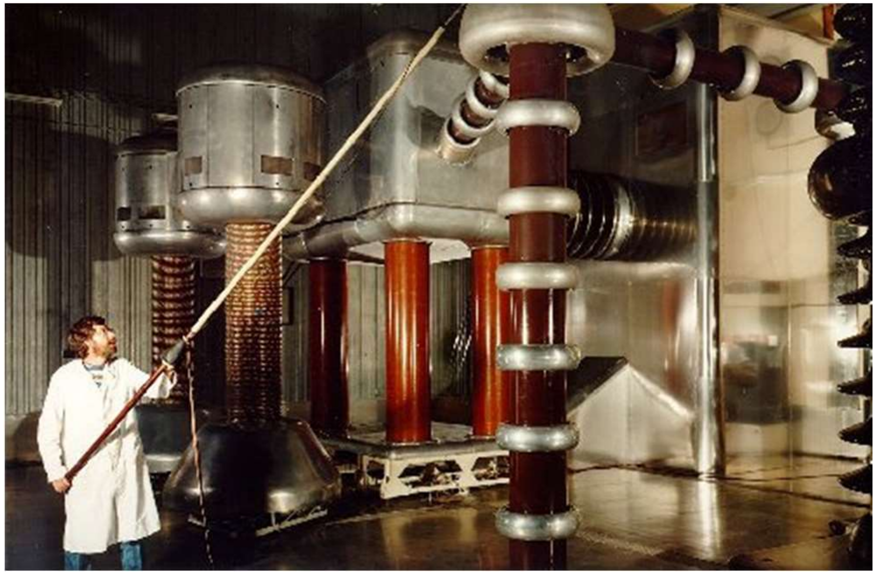
Martin Jehser, Clemens Rauer, Gerhard Zifferer
Marius, Reinecker, Wilfried Schranz

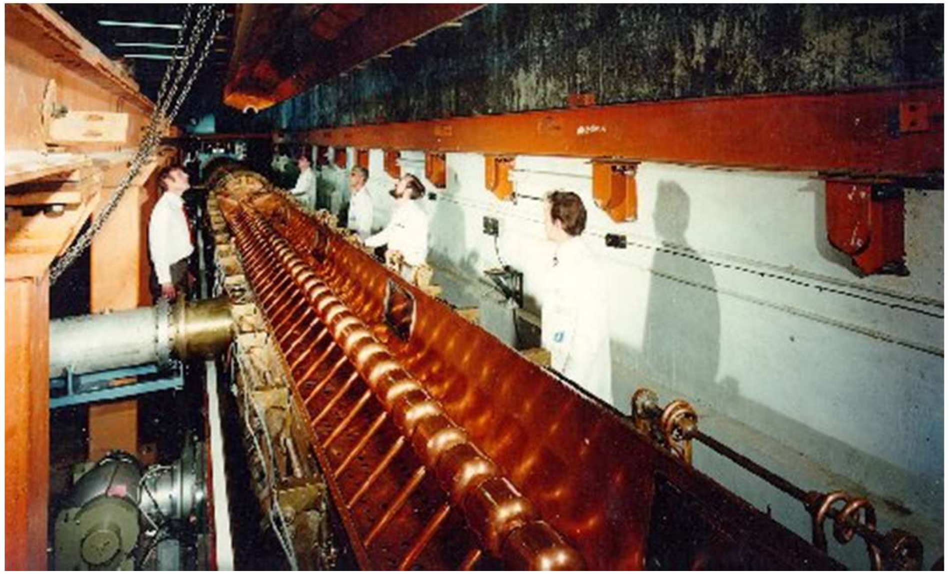
universität wien

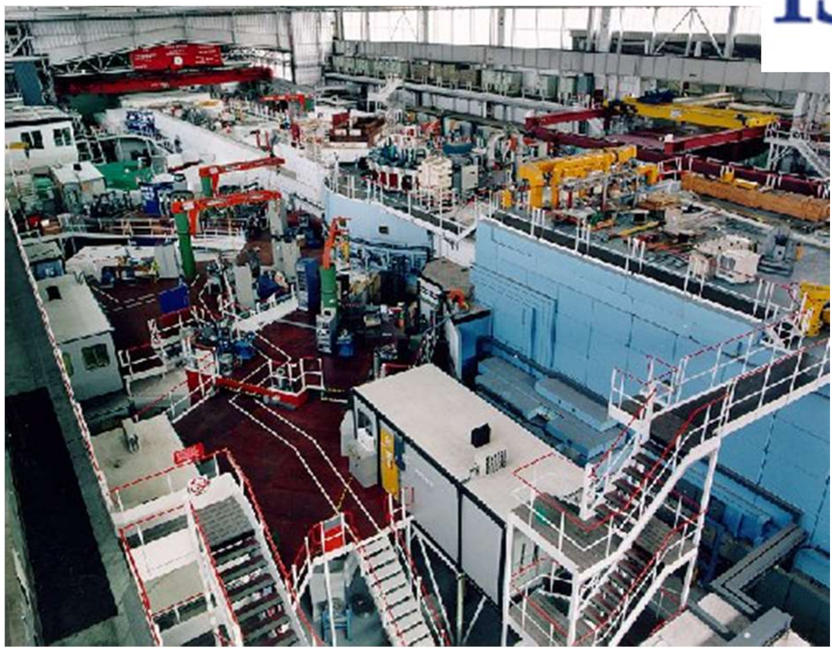
Amorphous ice

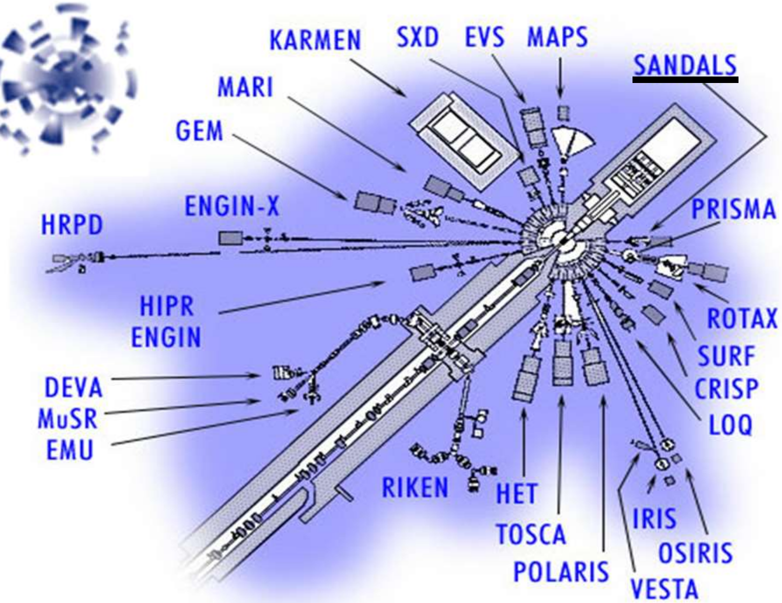


[1] E.F. Burton and W.F. Oliver, *Proc. R. Soc. A*, 153, 1935
[2] P. Brüggeller, E. Mayer, *Nature,* 288, 1980; E. Mayer, *J. Appl. Phys.,* 58, 1985
[3] O. Mishima, L.D. Calvert, E. Whalley, *Nature*, 310, 1984;
[4] O. Mishima, L.D. Calvert, E. Whalley, *Nature*, 314, 1985
[5] T. Loerting, C. Salzmann, I. Kohl, E. Mayer, A. Hallbrucker, *PCCP*, 3, 2001





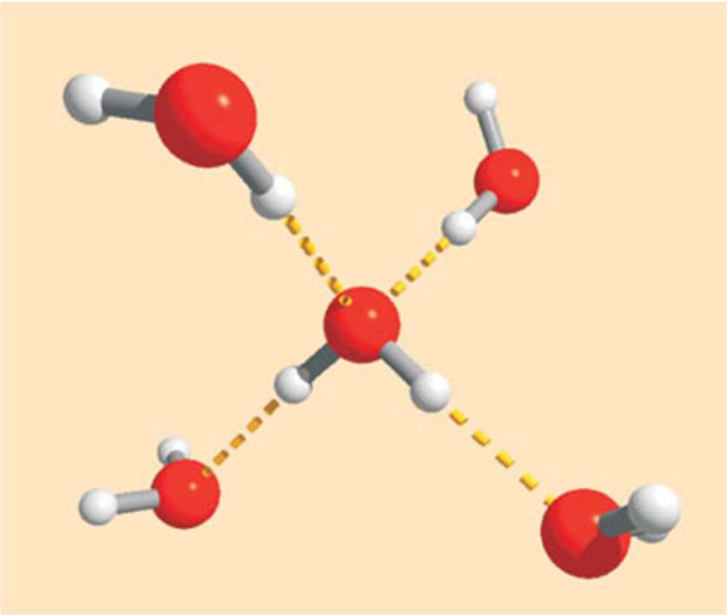


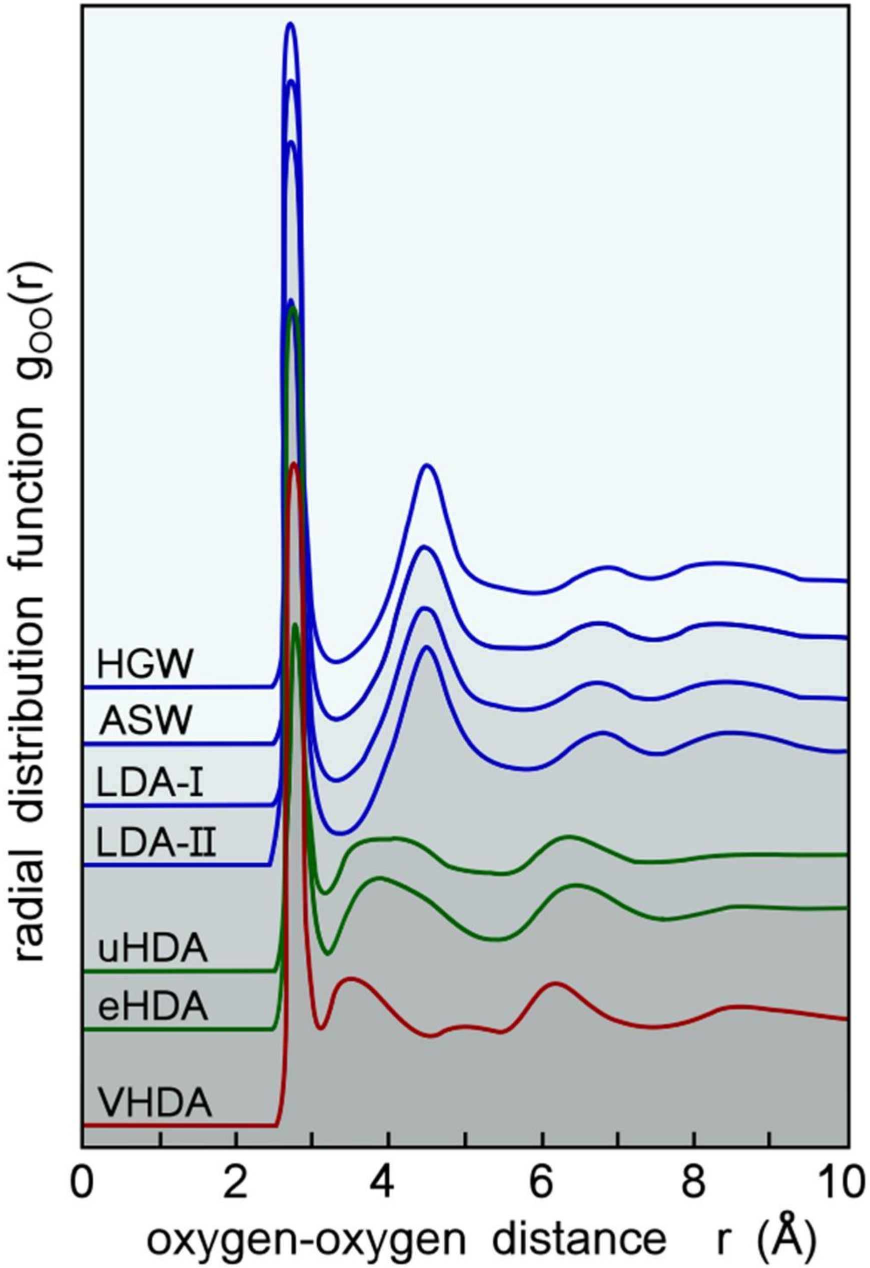


SANDALS -
Small Angle Neutron Diffractometer
for
Amorphous and Liquid Samples

Radial-Density Functions (rdfs)

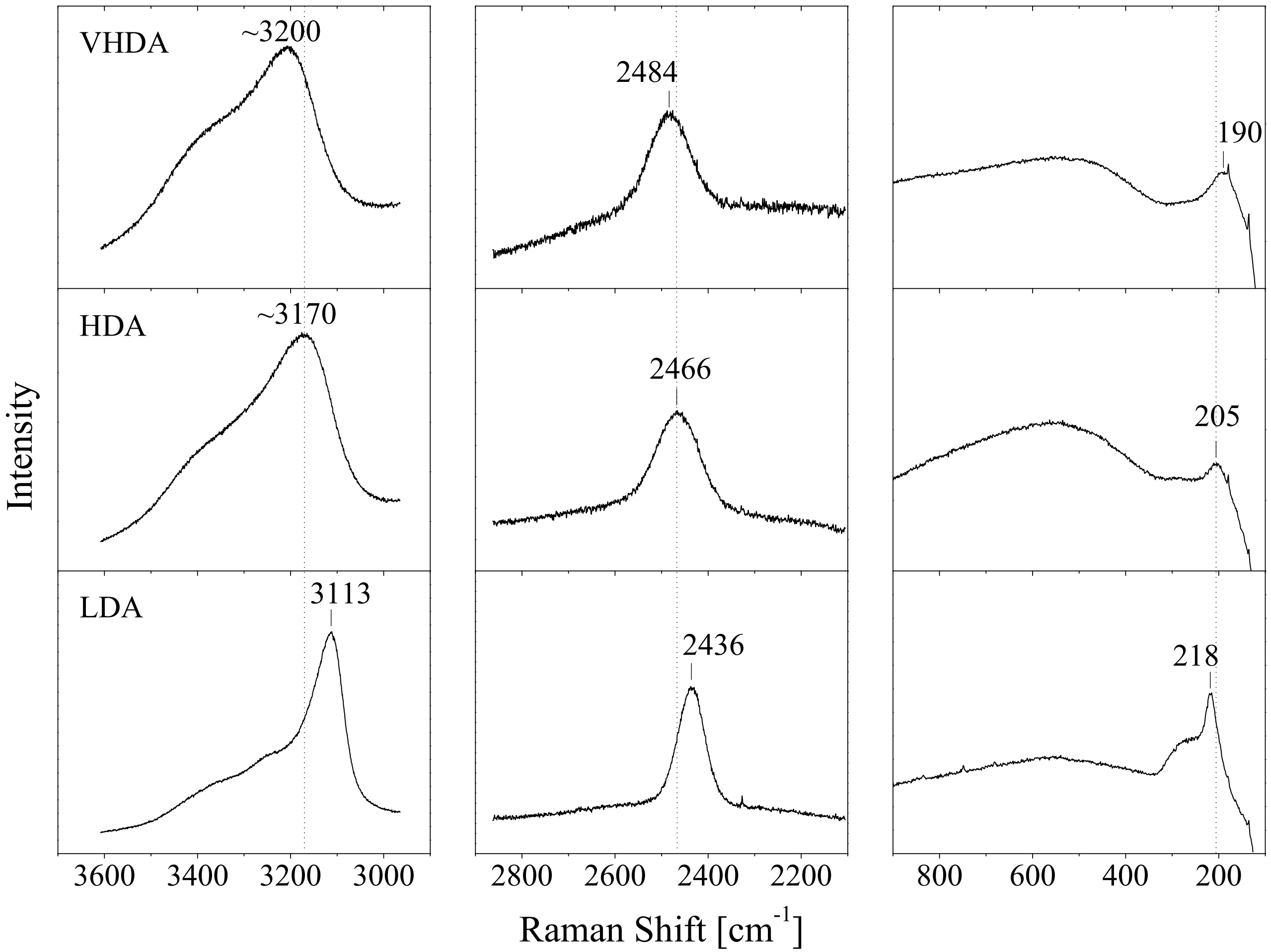
Coordination-Number:	
$H_2O_{(l)}$	4.3
hex. Ice	3.7
LDA	**3.9**
HDA	**5.0**
VHDA	**5.9**





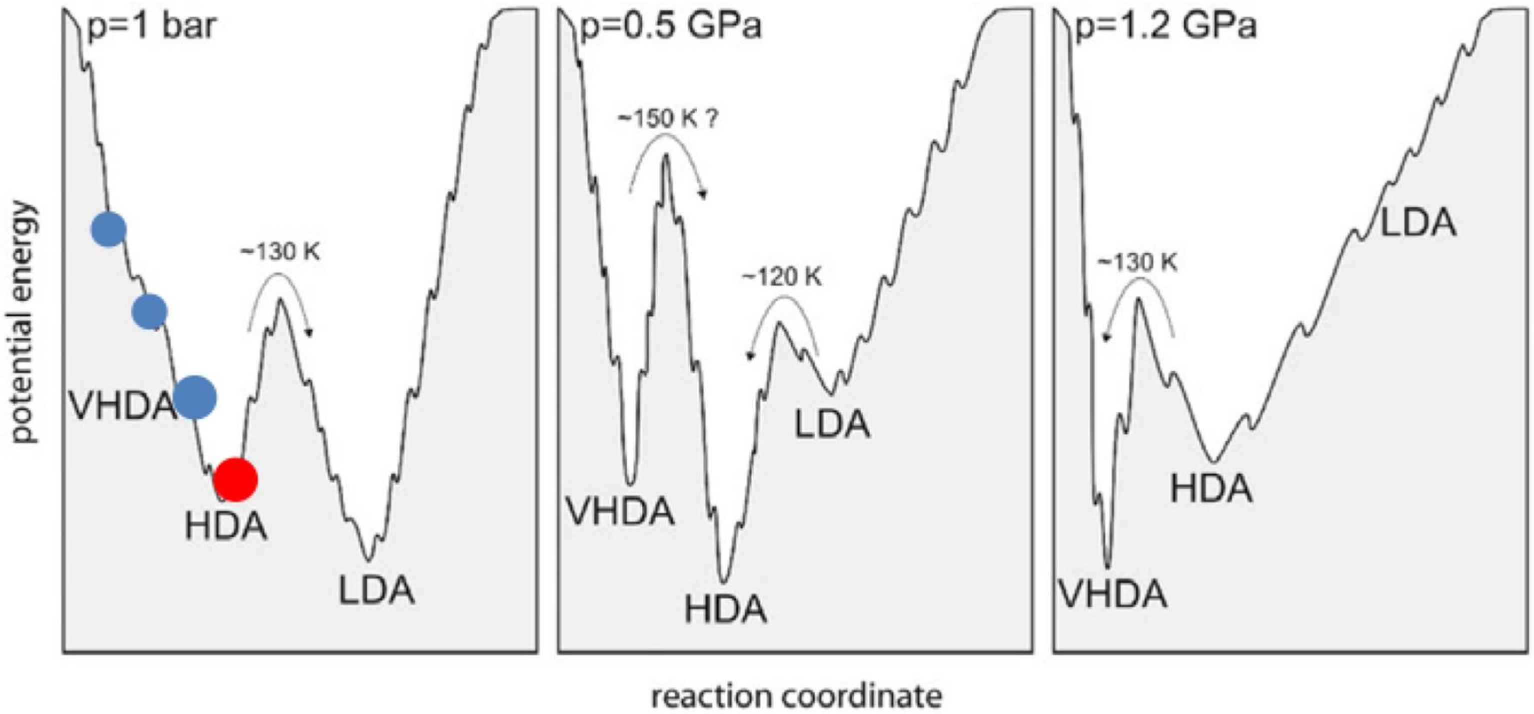
D. T. Bowron, J.L.Finney, A. Hallbrucker, I. Kohl, T. Loerting, E. Mayer, A. K. Soper, *J. Chem. Phys.* **125**, 194502 (2006)
J. L. Finney, Daniel T. Bowron, A. K. Soper, E. Mayer, A. Hallbrucker, T. Loerting, *Phys. Rev. Lett.* **89,** 205503(2002)

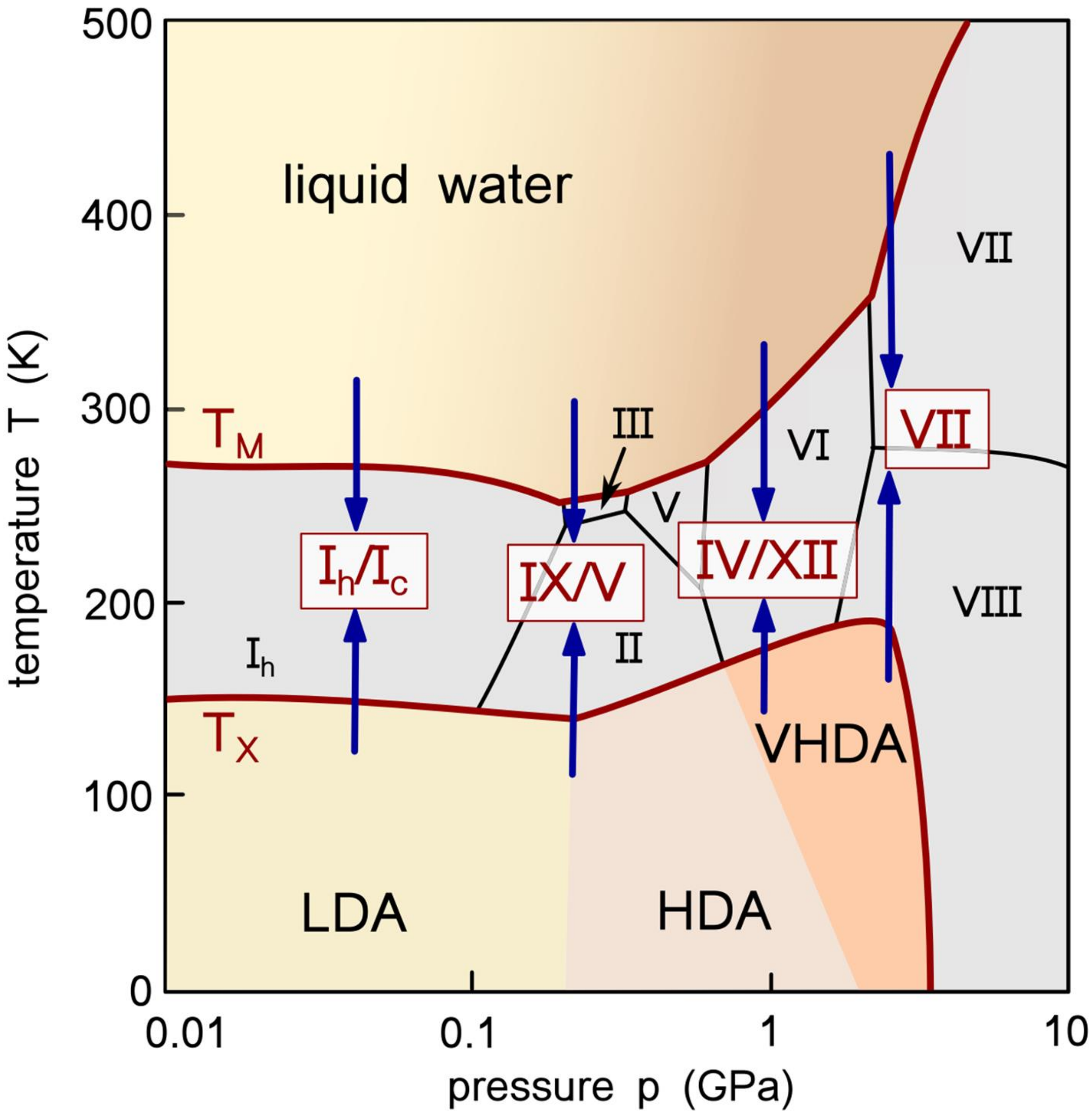
Raman-Spectroscopy (77 K)



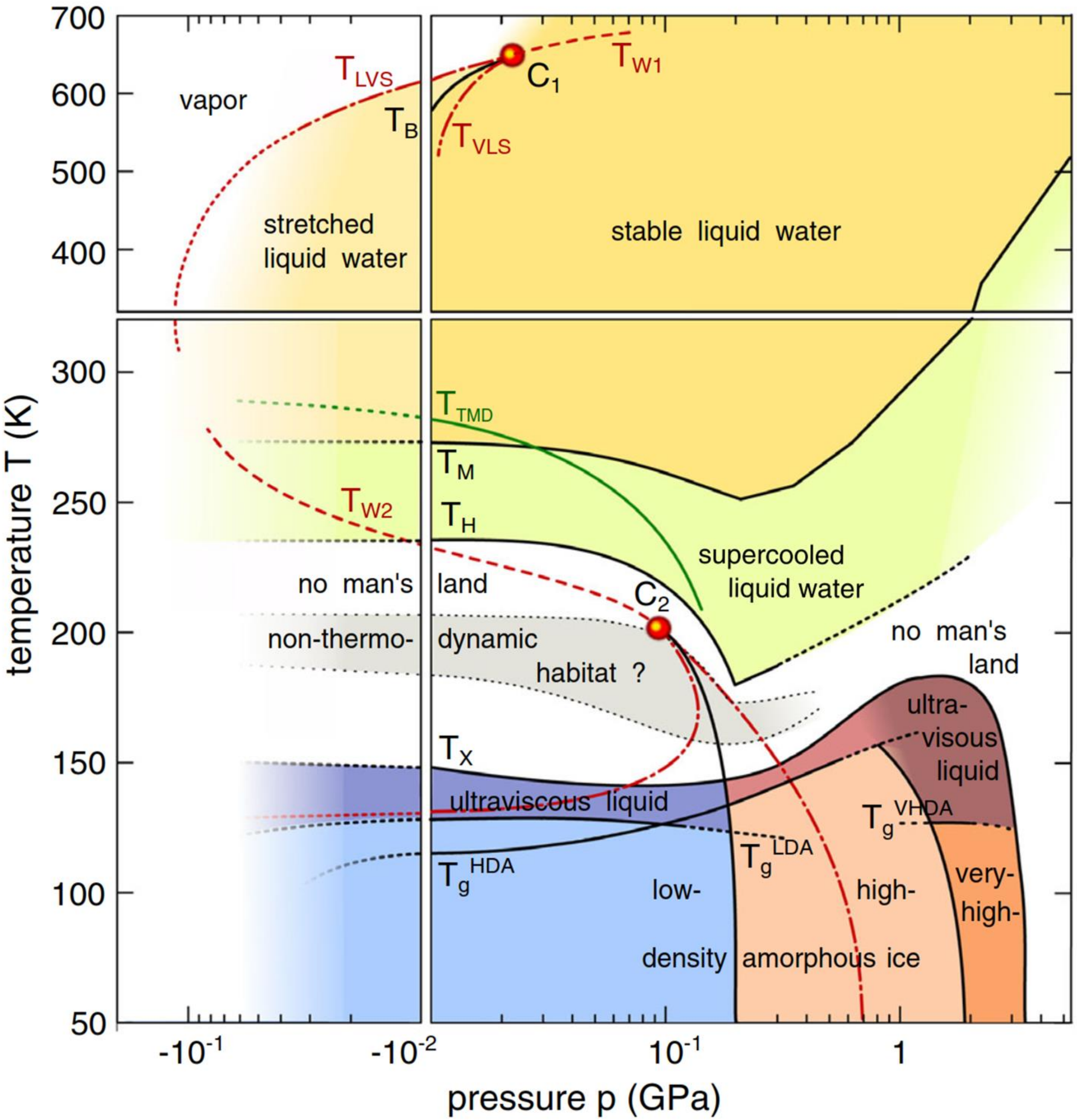
O – D ···· O distances:	LDA:	2.77 Å
	HDA:	2.82 Å
	VHDA:	2.85 Å

Relaxing amorphous ices at different pressures





liquid water
T_M
T_X
I_h/I_c
IX/V
IV/XII
VII
III
V
VI
VII
VIII
II
I_h
VHDA
LDA
HDA
500
400
300
200
100
0
0.01
0.1
1
10
temperature T (K)
pressure p (GPa)



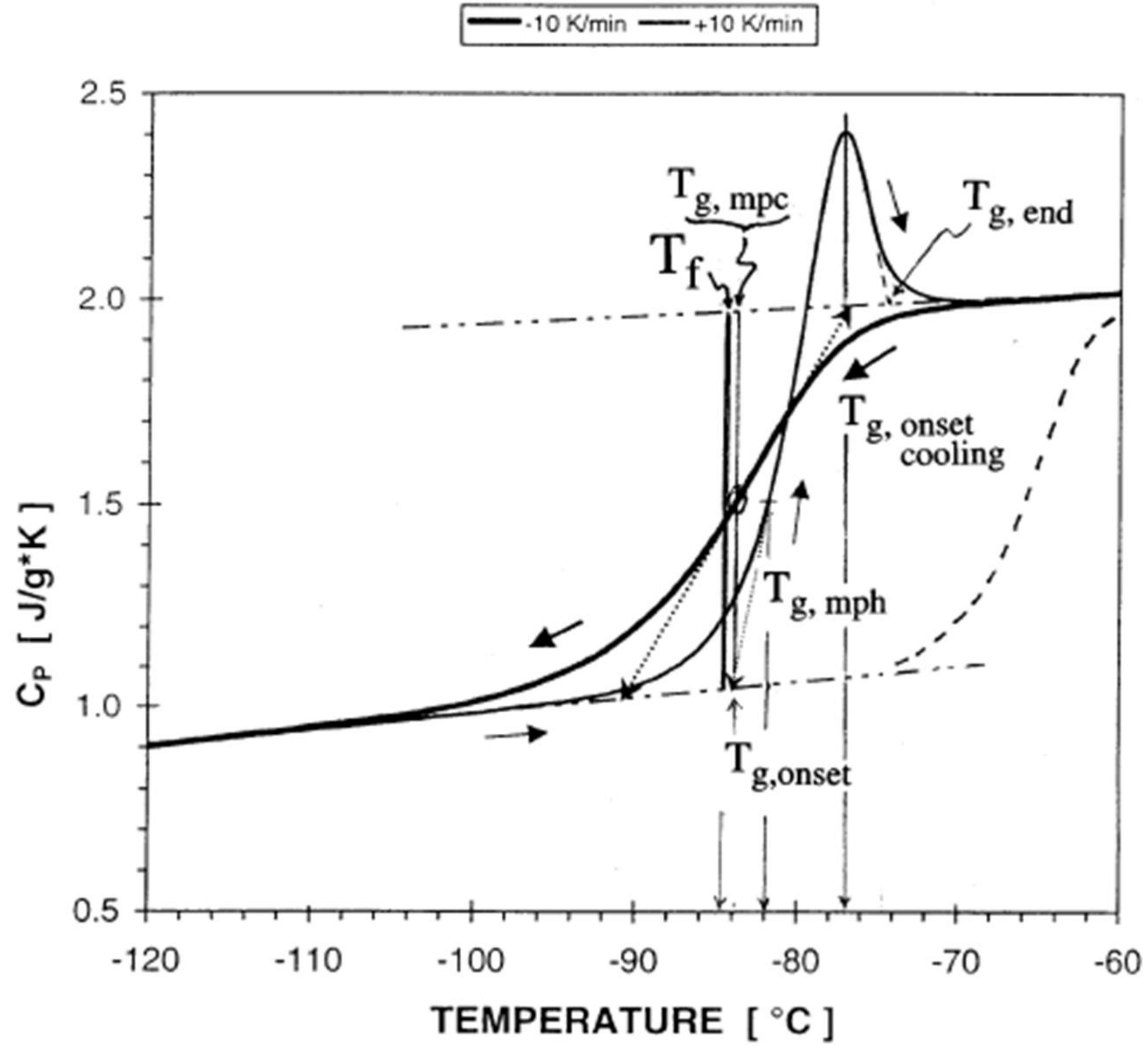
Amann-Winkel et al., **Rev. Mod. Phys.** *88* (2016) 011002.

RELAXATION DYNAMICS
GLASS TRANSITION

CALORIMETRIC GLASS TRANSITION

LDA

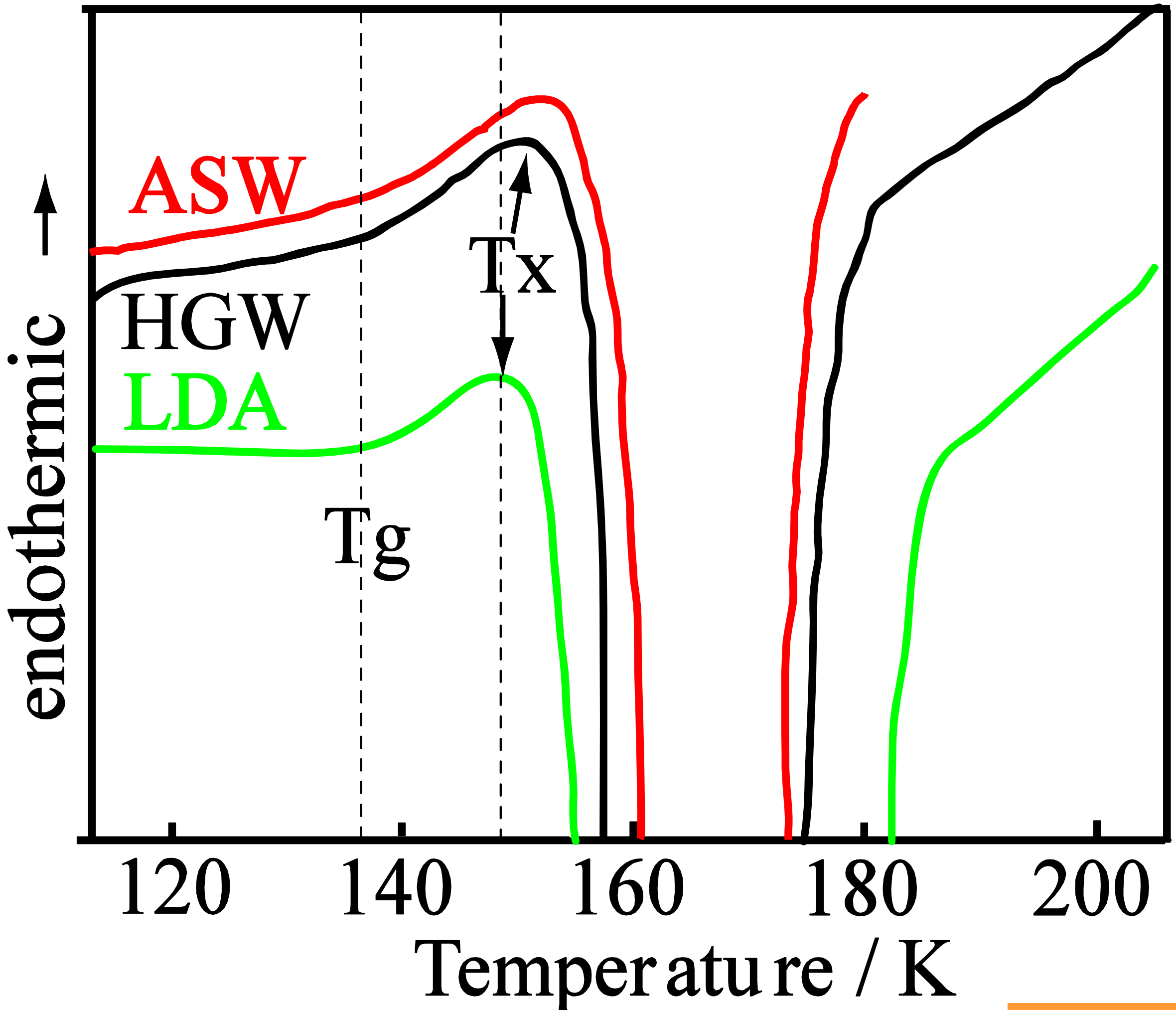
The Glass→Liquid transition



glycerol (DSC)

C.A. Angell, Chem.Rev. **102**, 2002

The glass transition at 136 K

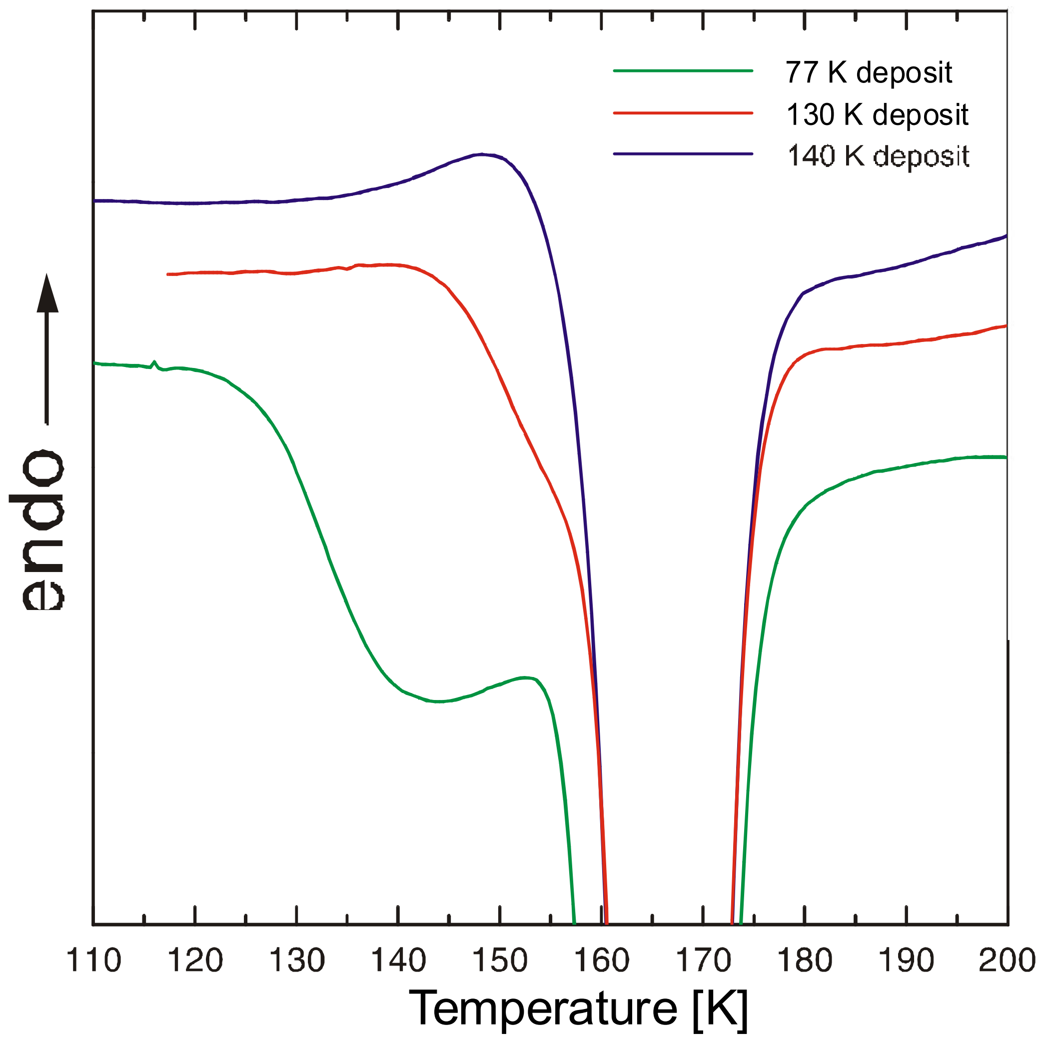


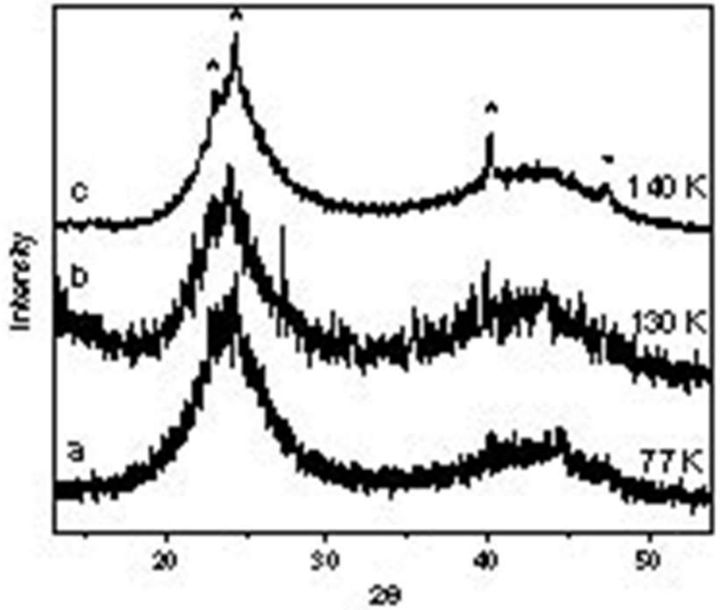
Johari et al., *Nature* **330** (1987) 552

Hallbrucker et al., *JPC* **93** (1989) 4986

ASW, HGW, LDA
Tg = 136 K
(heating rate: 30 K/min)

Glass Transition: HGW at 136 K





"Water Behaviour: Glass transition in hyperquenched water?", I. Kohl, L. Bachmann, A. Hallbrucker, E. Mayer, T. Loerting, **Nature** 435 (2005).

VOLUMETRIC GLASS TRANSITION

LDA - HDA

The Glass→Liquid transition

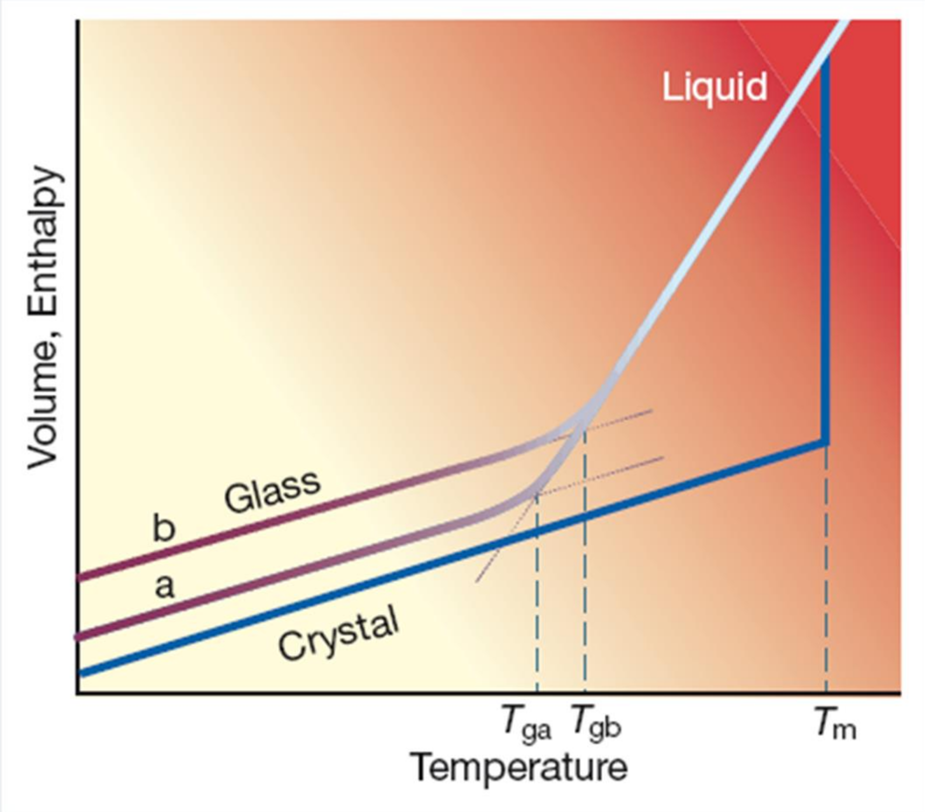
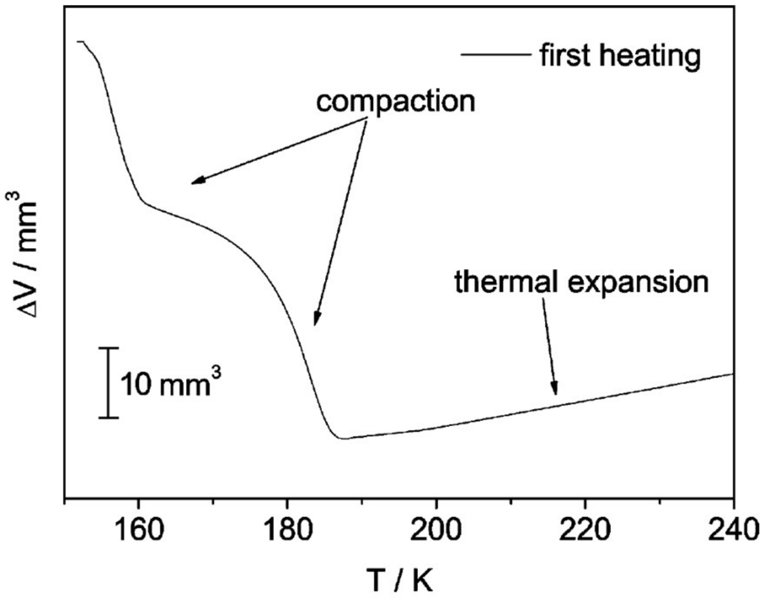
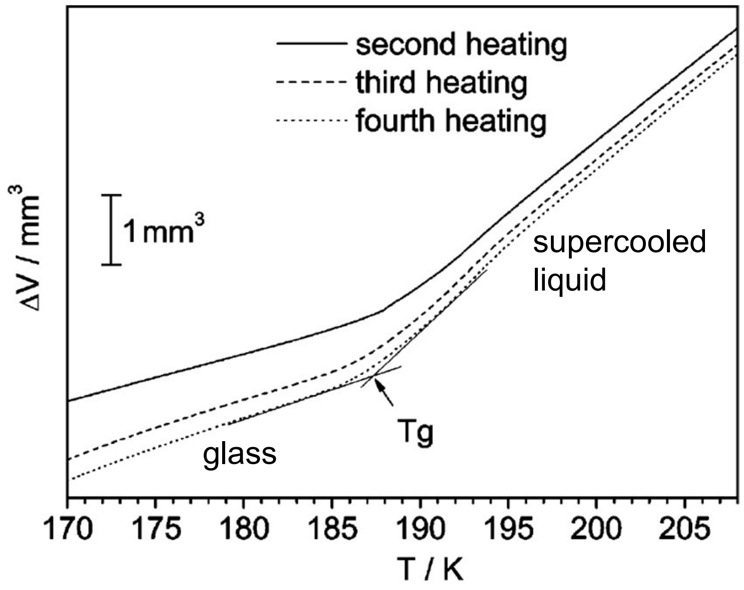


Figure 1 Temperature dependence of a liquid's volume *v* or enthalpy *h* at constant pressure. T_m is the melting temperature. A slow cooling rate produces a glass transition at T_{ga}; a faster cooling rate leads to a glass transition at T_{gb}. The thermal expansion coefficient $\alpha_p = (\partial \ln v / \partial T)_p$ and the isobaric heat capacity $c_p = (\partial h / \partial T)_p$ change abruptly but continuously at T_g.

Glycerol for benchmarking the method (0.05 GPa) [1]



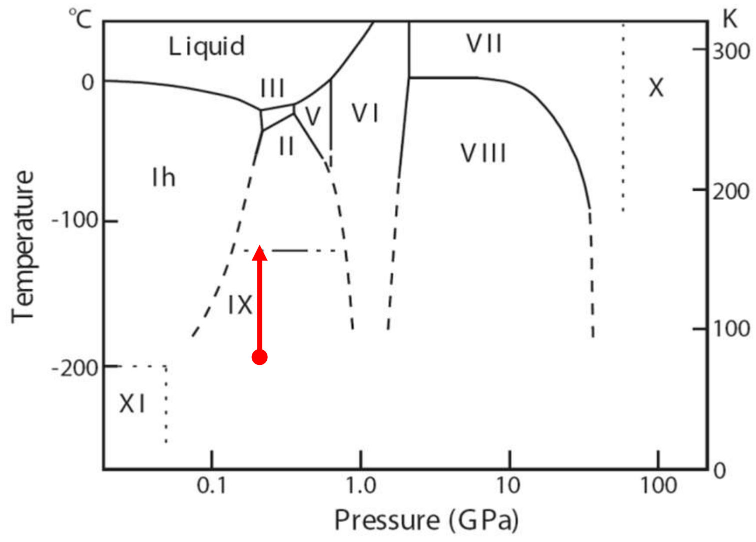
- heating rate: ≈1–3 K/min
- cooling rate: ≈25 K/min

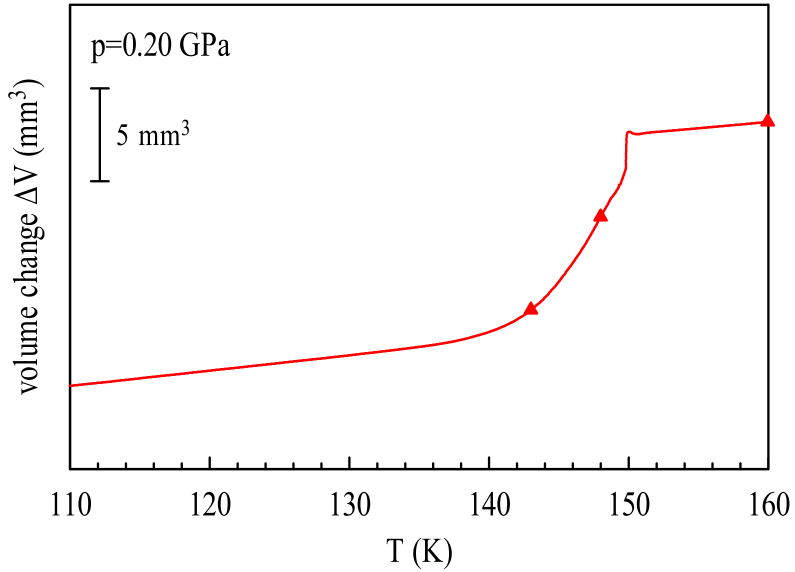


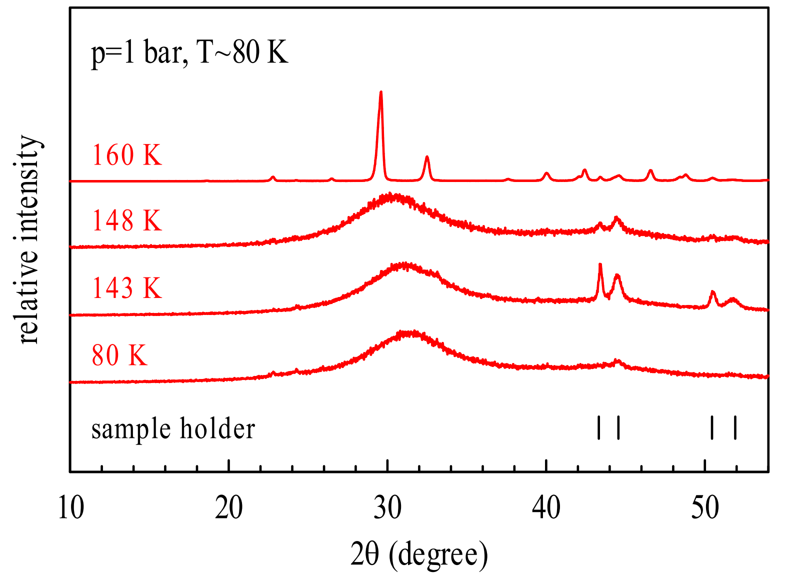
T_g ... glass transition temperature

[1] M. S. Elsaesser et al., **J. Phys. Chem. B** 111 (2007) 8038.

HDA: Volumetric measurements at 0.2 GPa







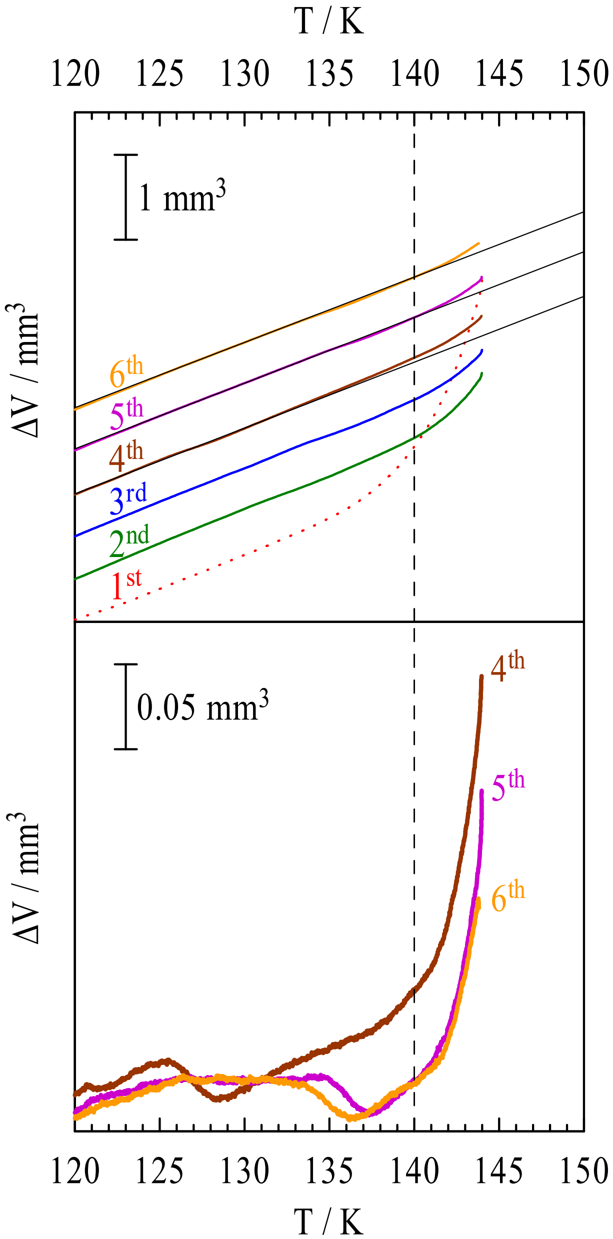
Full crystallization (160 K):

eHDA → ice IX

Onset of crystallization >148 K

M. Seidl et al., PRB, **83**, 2011

HDA: Volumetric glass transition at 0.2 GPa



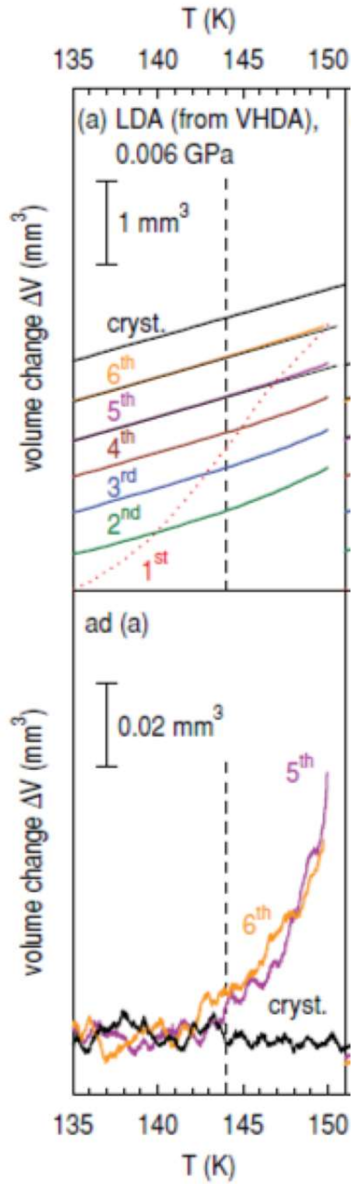
Reversibility:
sample was heated 6x to 144 K

Heating rate: 2 K/min
Cooling rate: 2 K/min

Onset of volumetric Tg:
= deviation from linearity

M. Seidl et al., PRB, **83**, 100201, 2011

LDA: Volumetric glass transition at 0.006 GPa

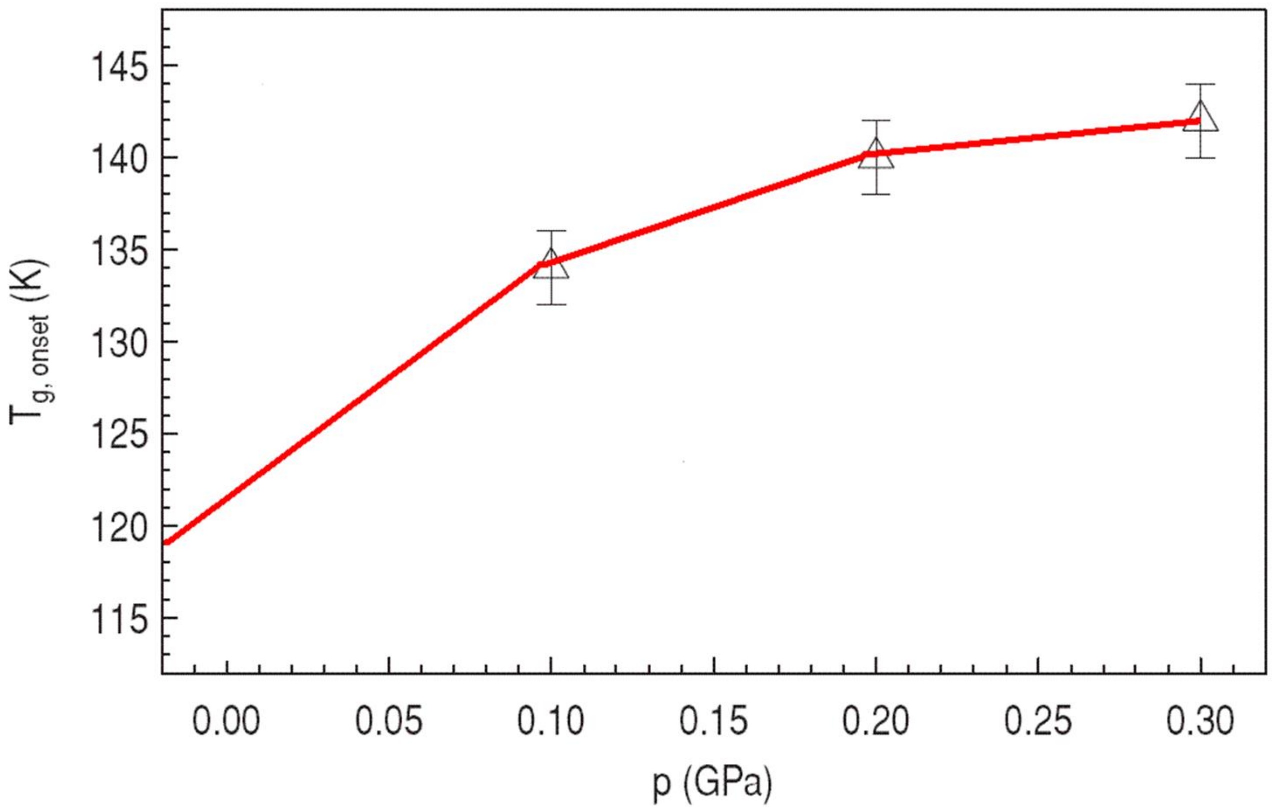


Reversibility:
sample was heated 6x to 149 K

Heating rate: 2 K/min
Cooling rate: 2 K/min

Onset of volumetric Tg:
= deviation from linearity

Pressure dependence of the glass transition in HDA

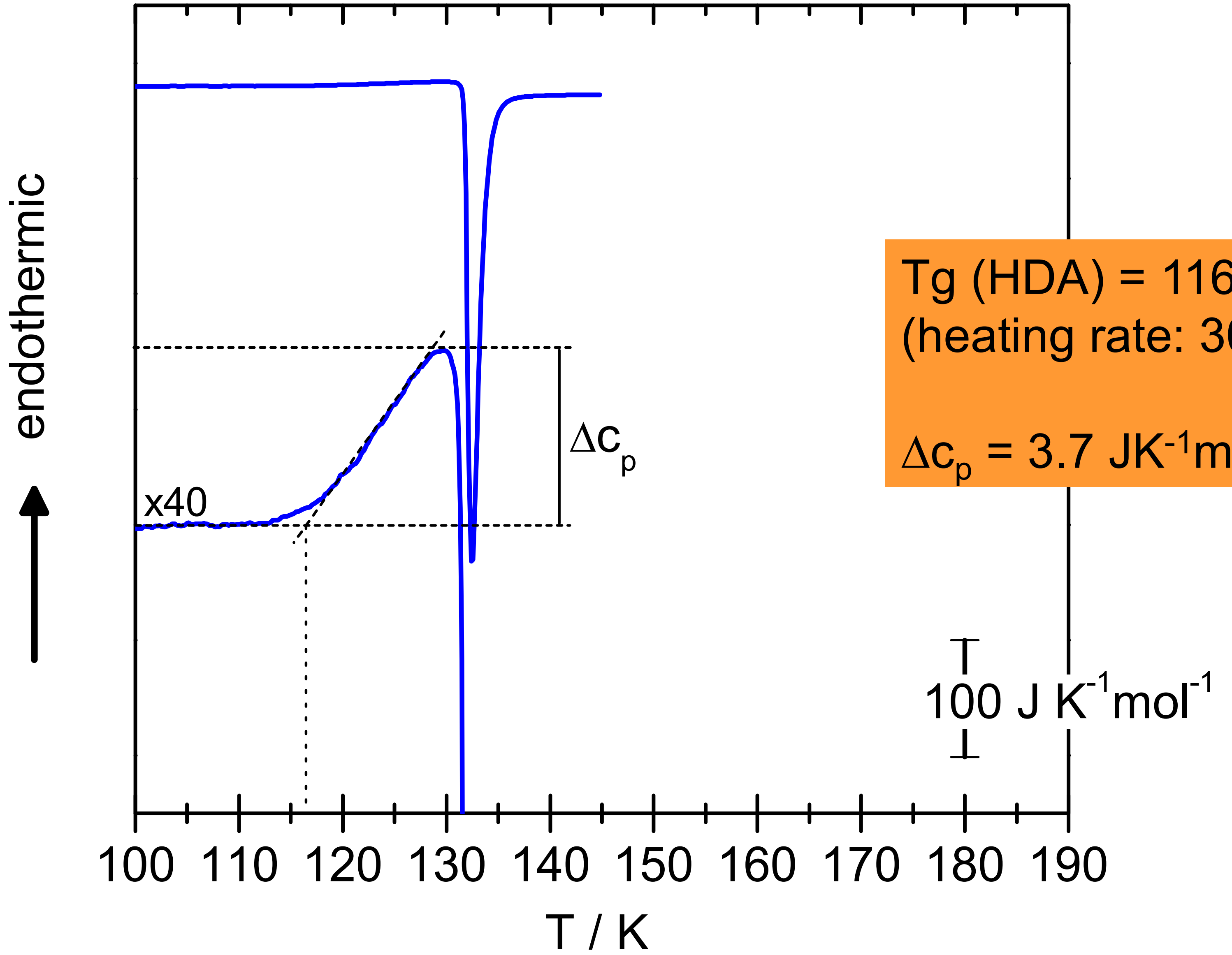


M. Seidl et al., PRB, **83**, 100201, 2011

CALORIMETRIC GLASS TRANSITION

HDA

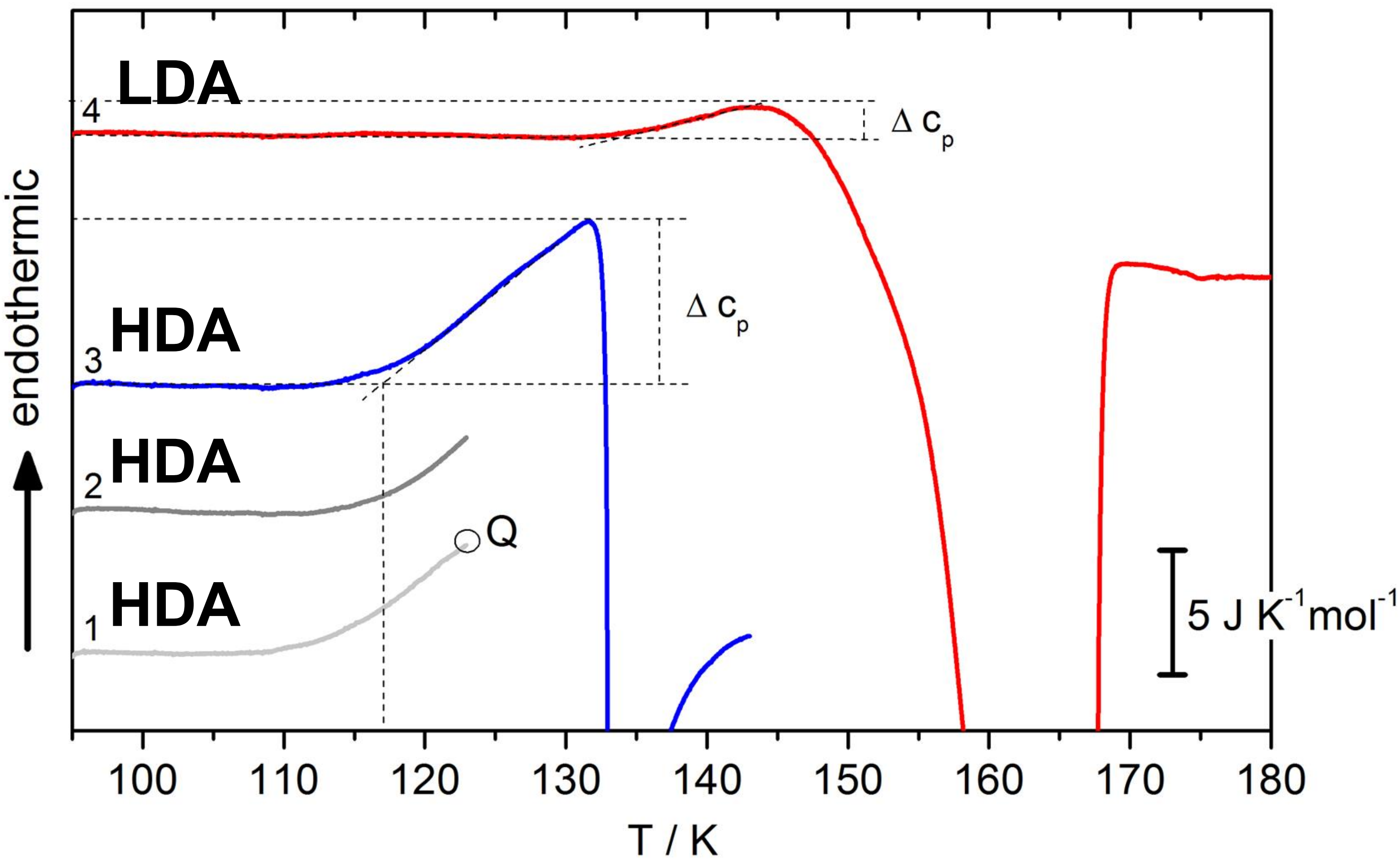
The glass → liquid transition : HDA – HDL

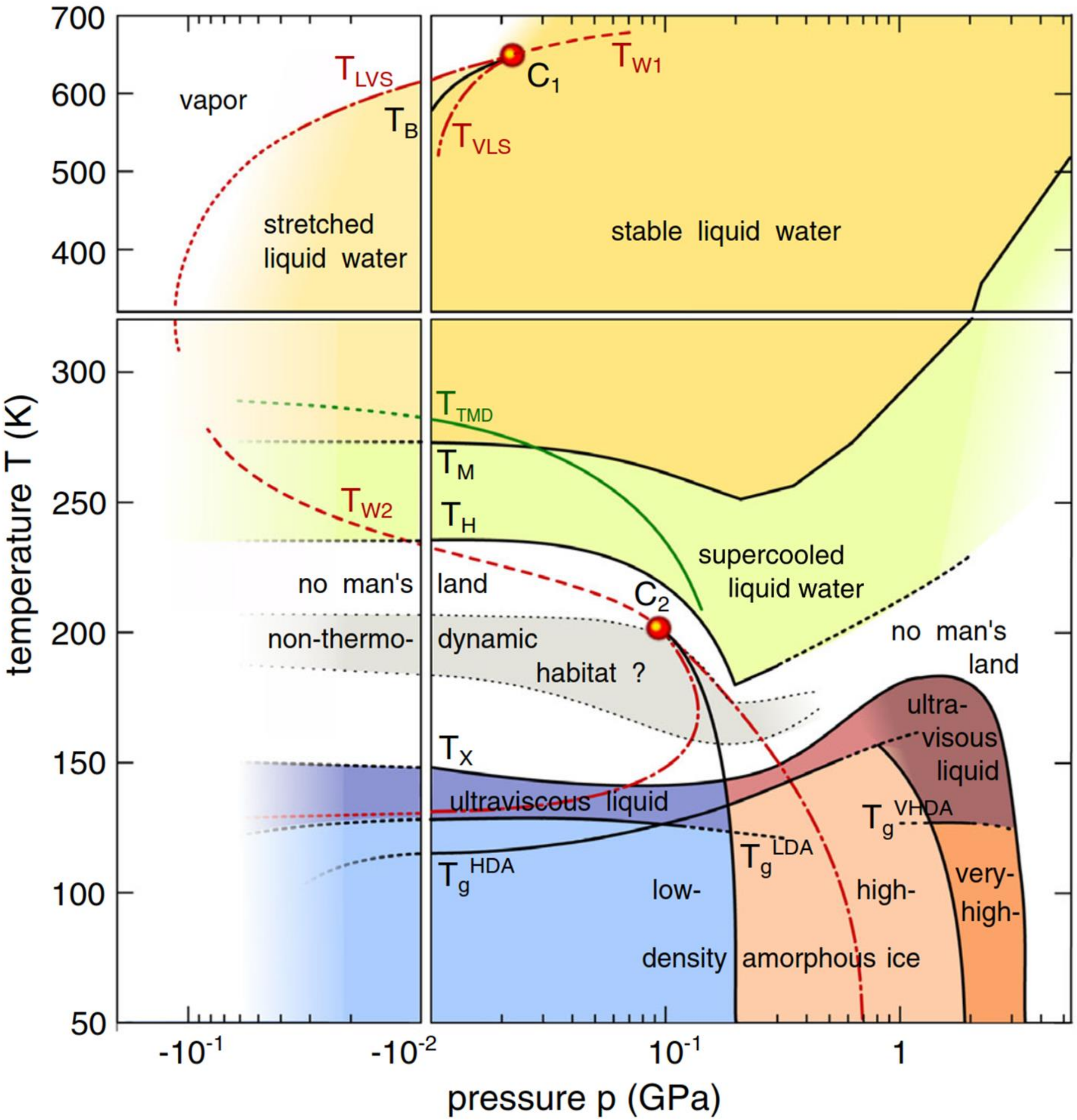


Tg (HDA) = 116 K
(heating rate: 30 K/min)

Δc_p = 3.7 $JK^{-1}mol^{-1}$

Two Glass Transitions in Water





Amann-Winkel et al., **Rev. Mod. Phys.** *88* (2016) 011002.

- Two calorimetric glass transitions in water

ΔCp very small

???

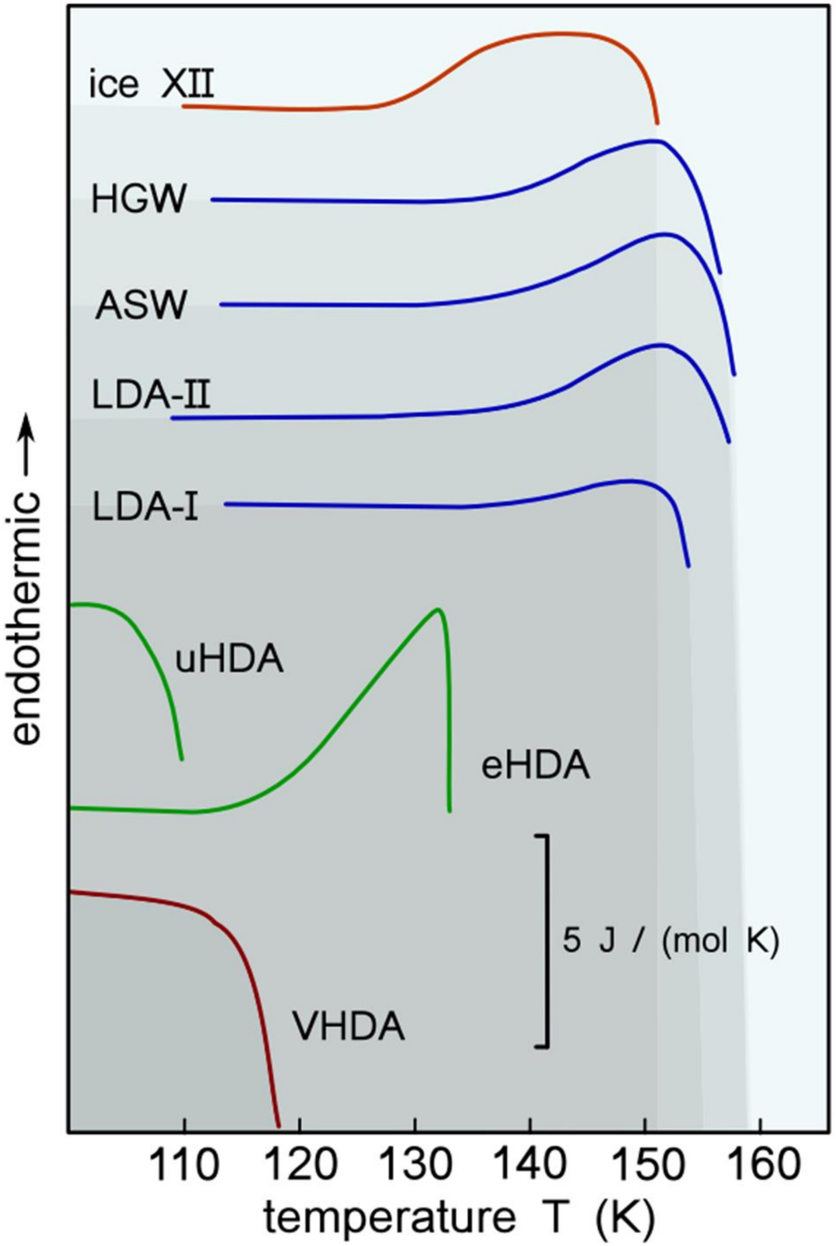
Glass-Liquid Transition at Tg ???

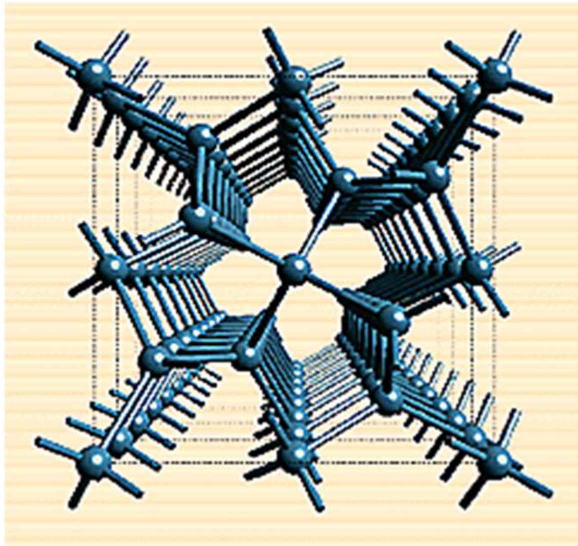
Solid-Solid Transition at Tg ???

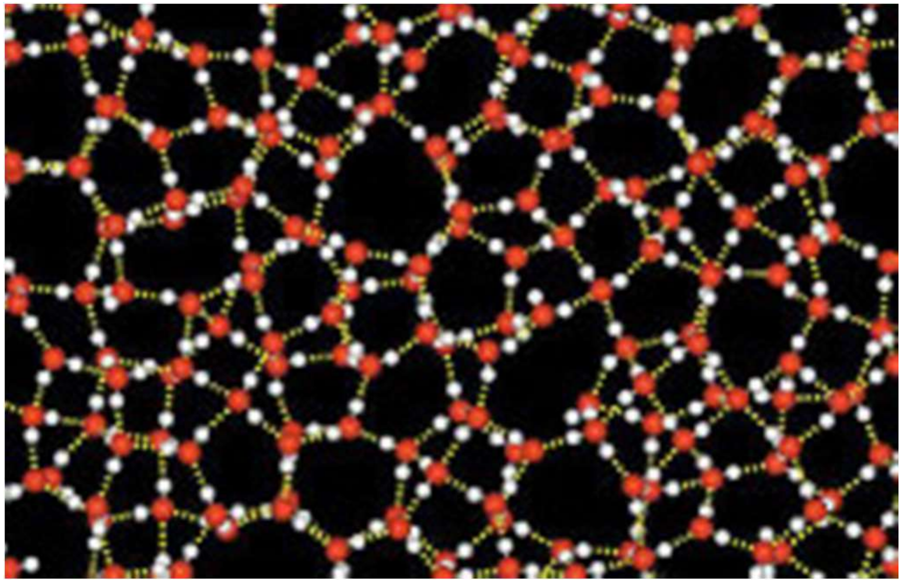
- Dielectric measurements at 1 kHz
  (Johari, Hallbrucker, Mayer, JCP 95, 1991)
- ASW – isotope intermixing in thin films: Tg < Tx (160 K)
  (Smith, Kay, Nature 398, 1999)
- Glass-forming aqueous mixtures
  (Capacciolo, Ngai, JCP 135, 2011)
- Penetration of LDA
  (Johari, JPCB 102, 1998)

- „shadow“ of the real glass transition
  (Yue, Angell, *Nature* 427, 2004)
- Tg of the proton sub-lattice
  (Fisher, Devlin, JPC 99, 1995
  Salzmann et al., PCCP 13, 2011)
- Impurity/Interface Effect
  (McCartney/Sadtchenko, JCP 138 2013
  Chonde/Brinzda/Sadtchenko JCP 125 2006)

Calorimetric glass transitions in water

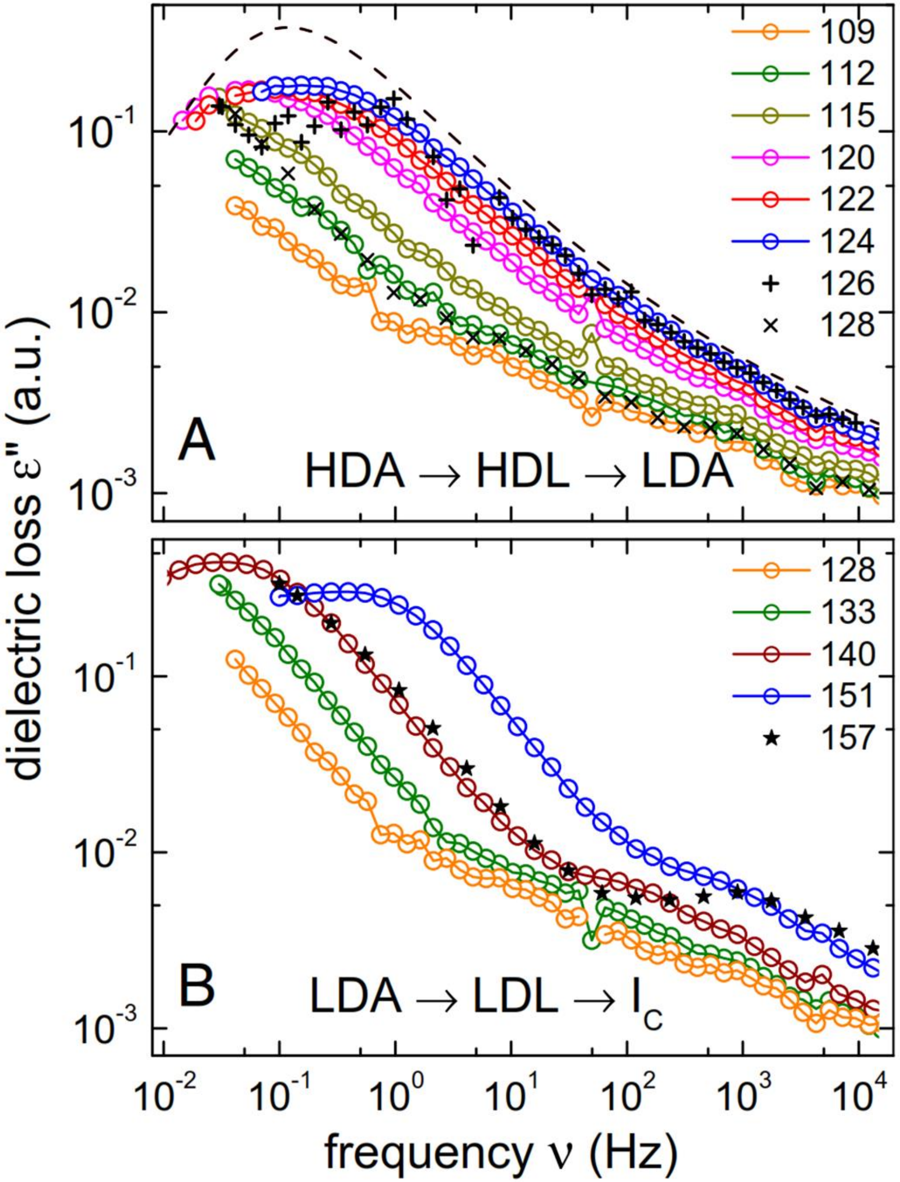




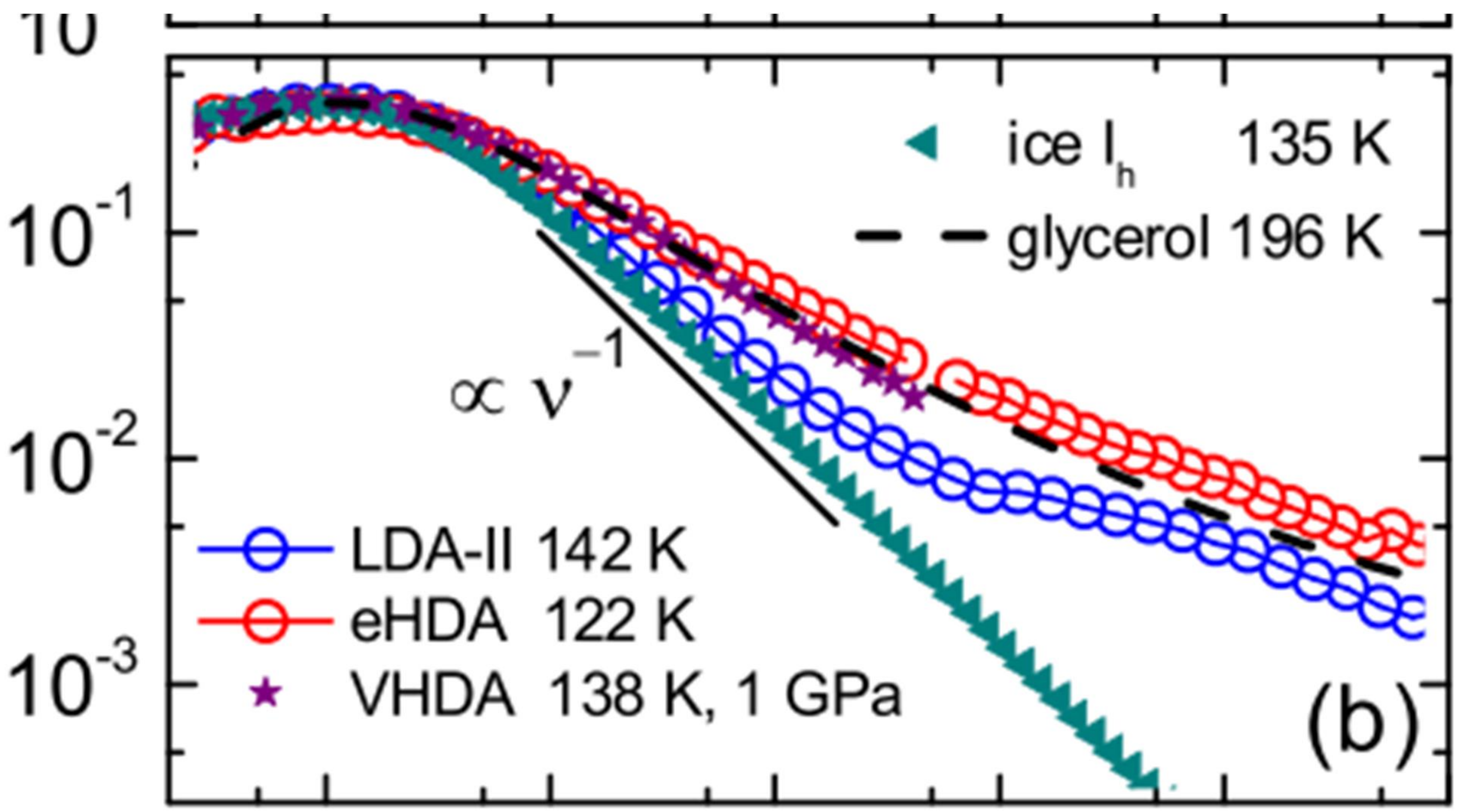


DIELECTRIC
GLASS TRANSITION

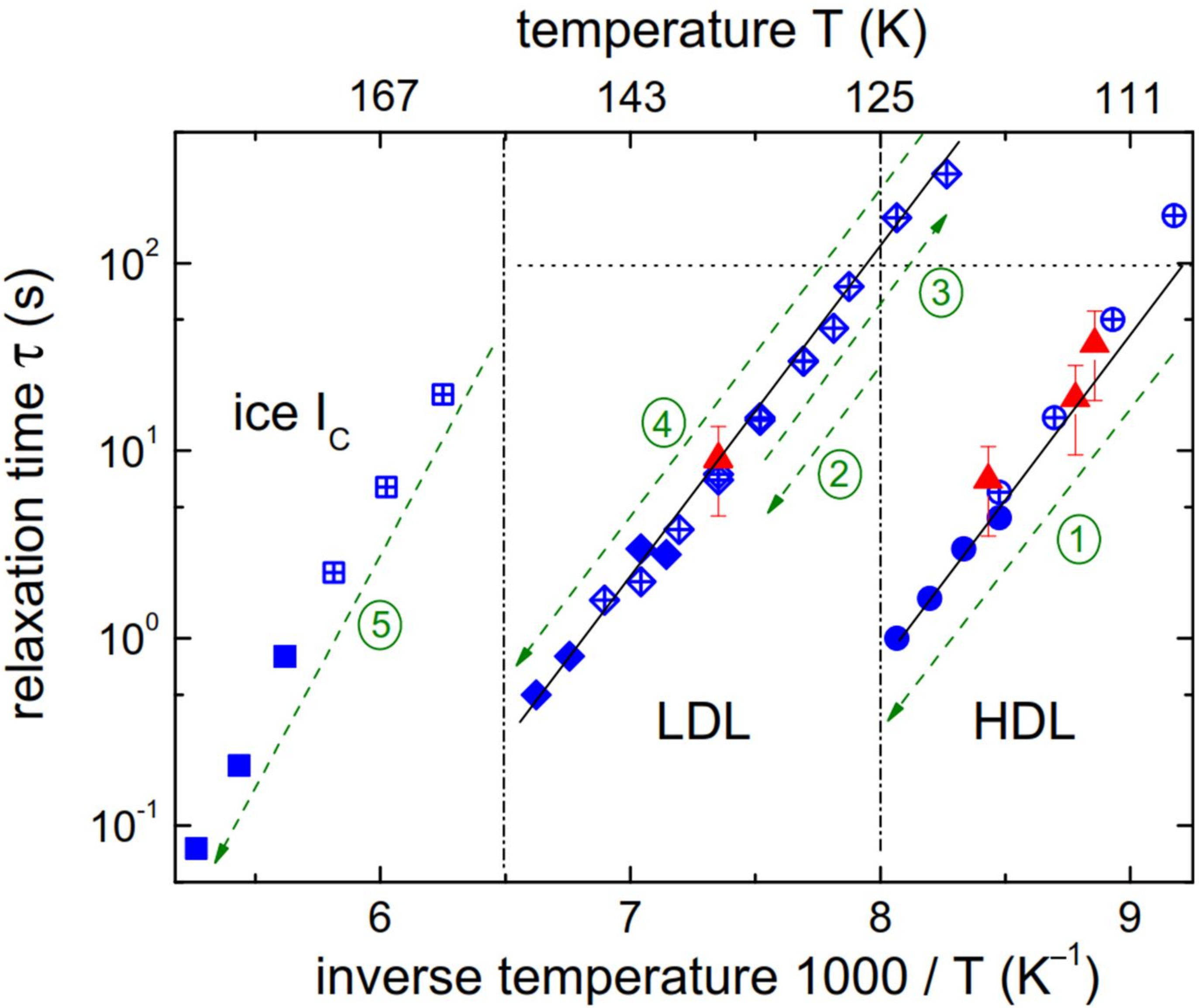
LDA - HDA



Amann-Winkel et al. **Proc. Natl. Acad. Sci. U.S.A.** *110* (2013) 17720–17725.



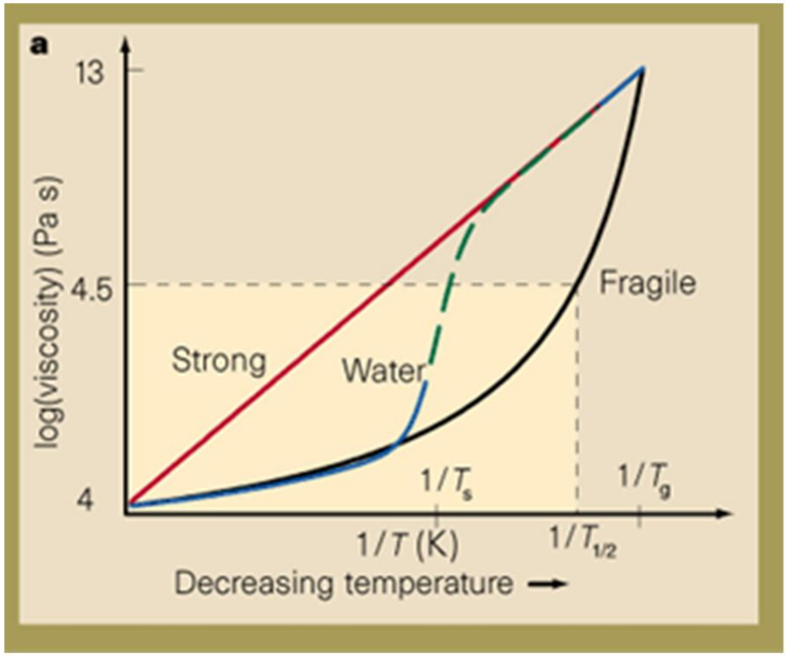
Amann-Winkel et al. **Proc. Natl. Acad. Sci. U.S.A.** *110* (2013) 17720–17725.

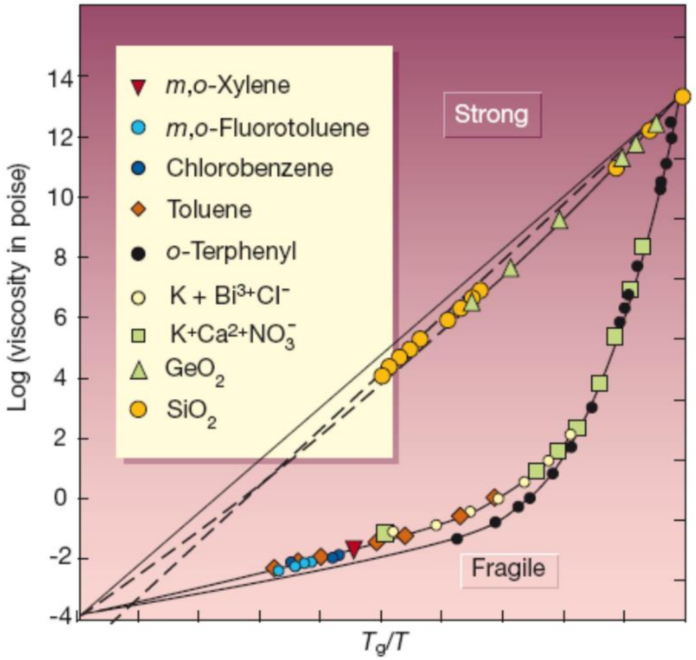


Fragility: LDL „superstrong“ m=14

HDL „strong“ m=20-25

Fragile-Strong Transition



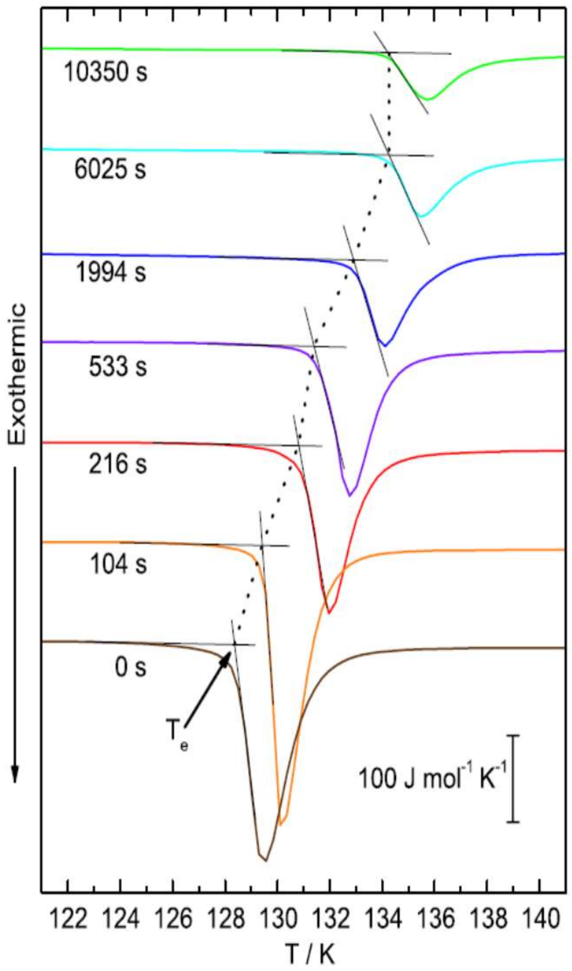


P.G. Debenedetti, F.H. Stillinger, *Nature* ***410***, 259 – 267, 2001

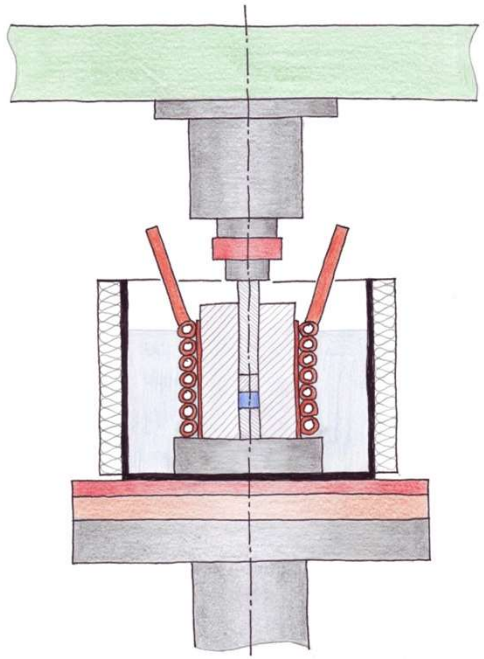
STRUCTURAL RELAXATION TIMES

HDA - VHDA

Relaxing/Equilibrating HDA



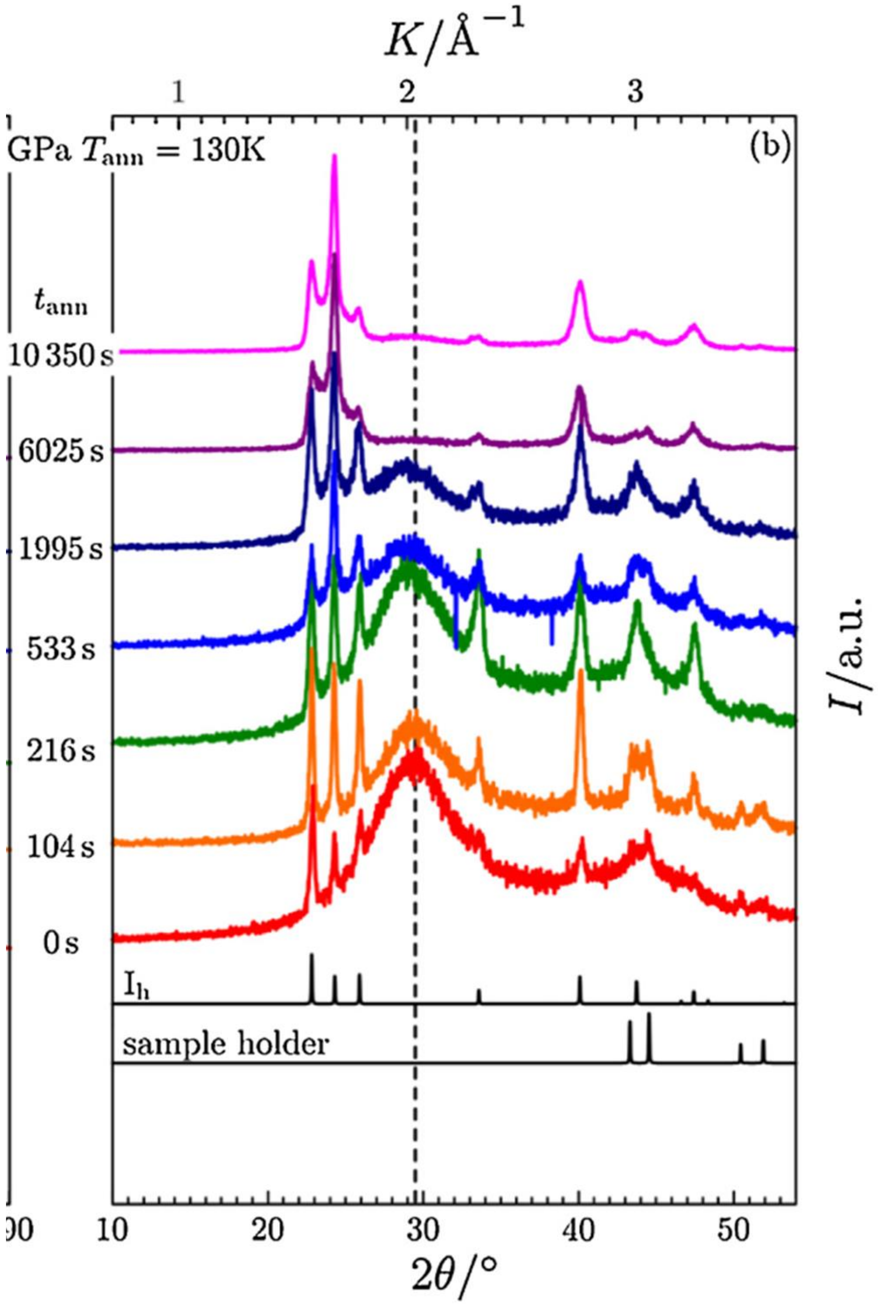
Isothermal/isobaric waiting experiment at 0.1 GPa/130 K



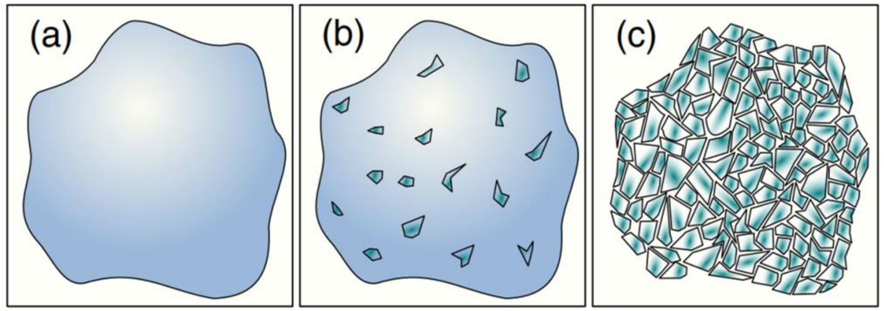
$$T_e(t) = T_{e,\infty} + (T_{e,0} - T_{e,\infty})e^{-(t/\tau)^n}$$

τ = 2980 s

Handle, Seidl, Loerting, PRL, **108** (2012) 225901

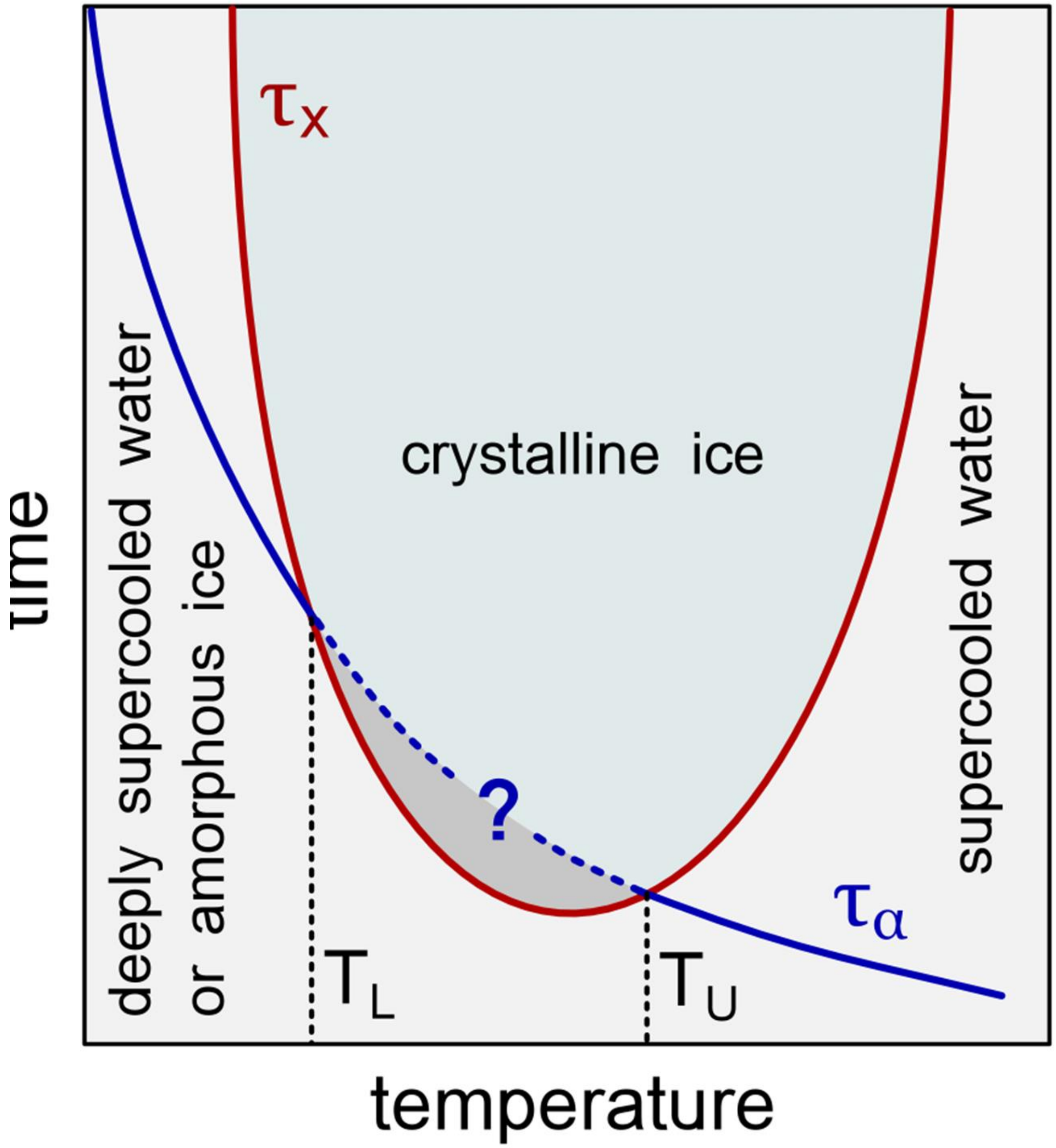


K/Å^{-1}
1
2
3
GPa T_{ann} = 130K
(b)
t_{ann}
10 350 s
6025 s
1995 s
533 s
216 s
104 s
0 s
I_h
sample holder
I/a.u.
10
20
30
40
50
2θ/°



(a)
(b)
(c)

uHDA

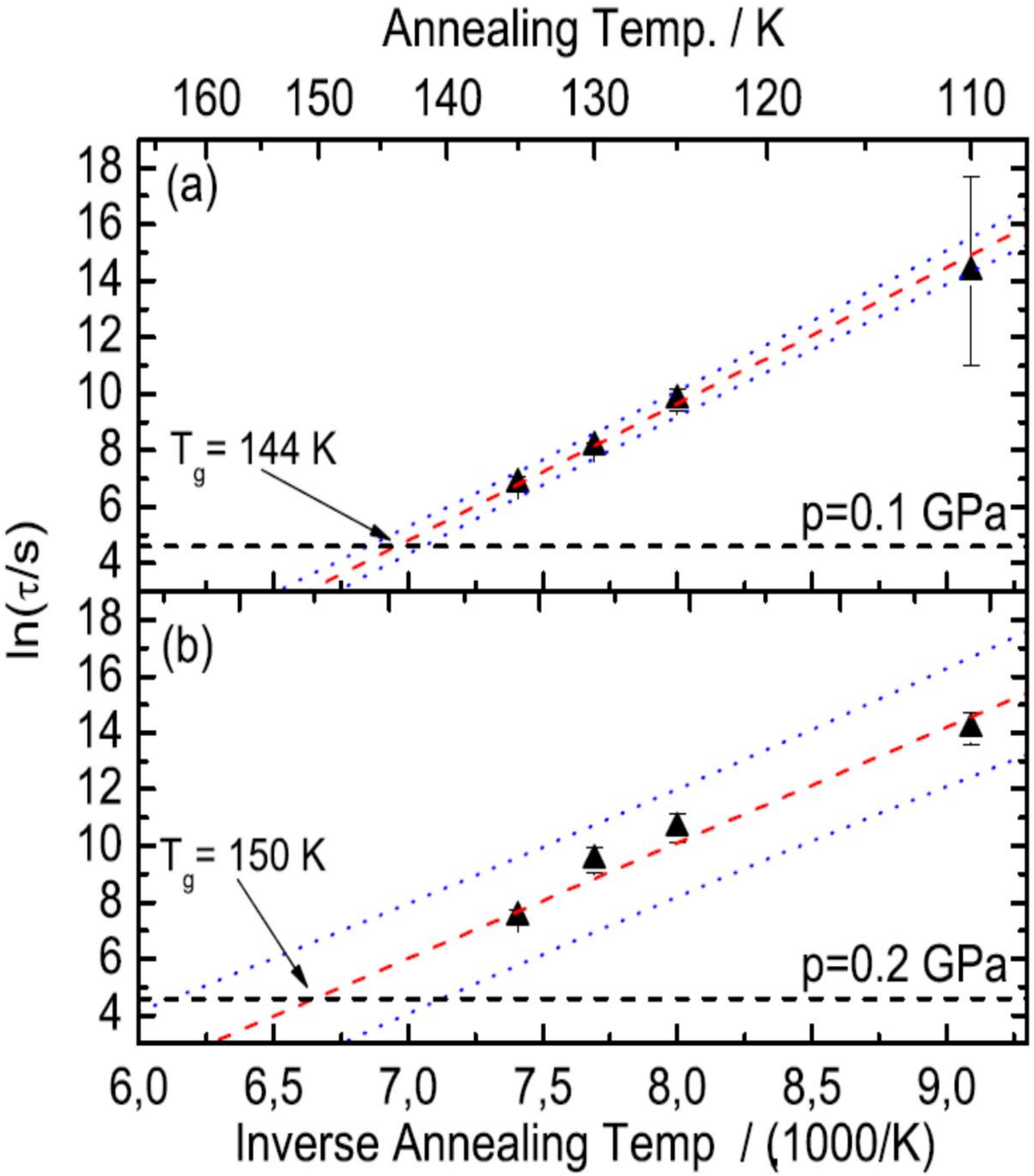


uHDA can be equilibrated at 130 K/0.1 GPa;

eHDA = eqHDA

timescale: one hour (i.e., solid)

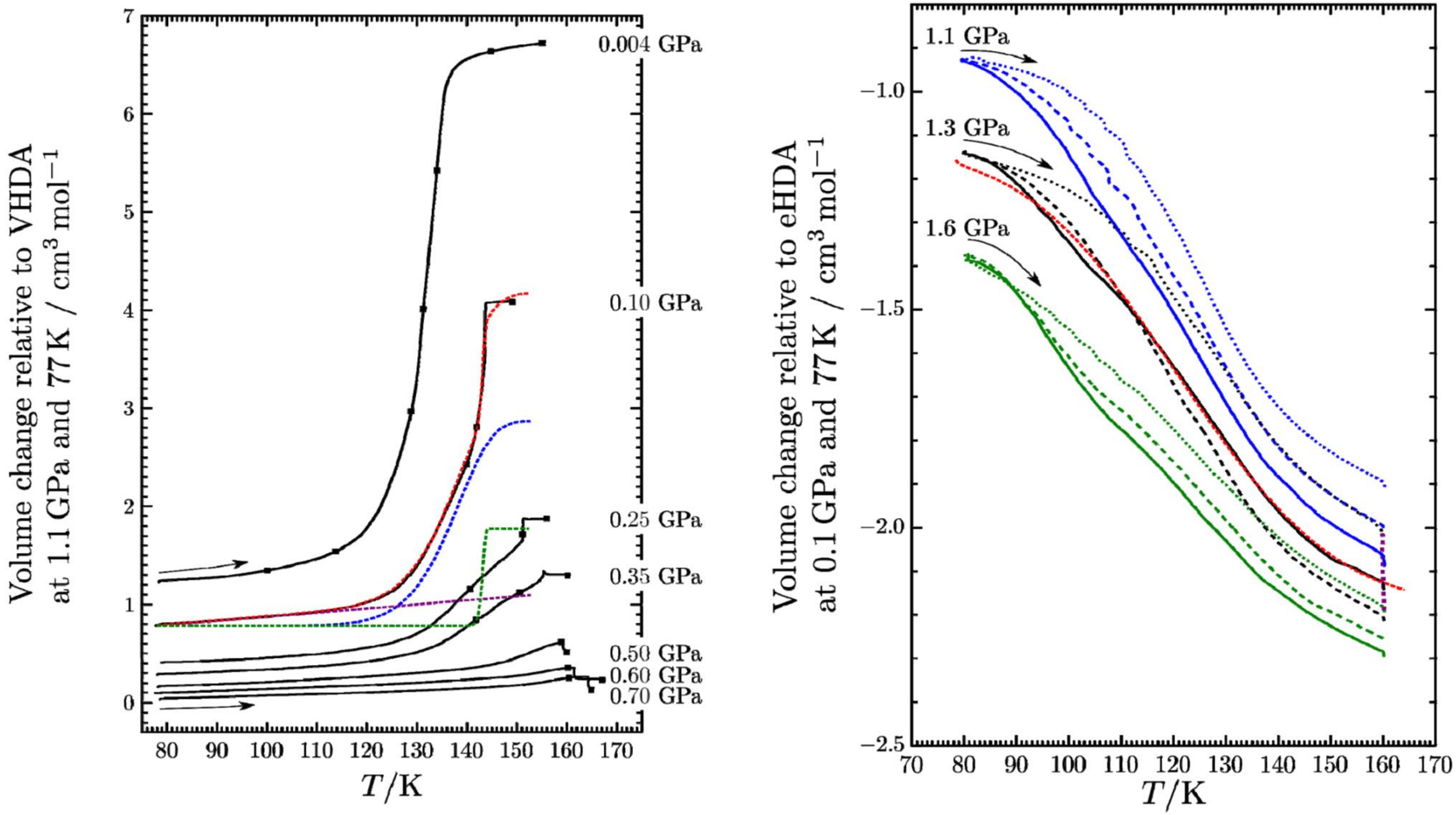
uHDA cannot be equilibrated at 145 K/0.1 GPa (interference of crystal growth)



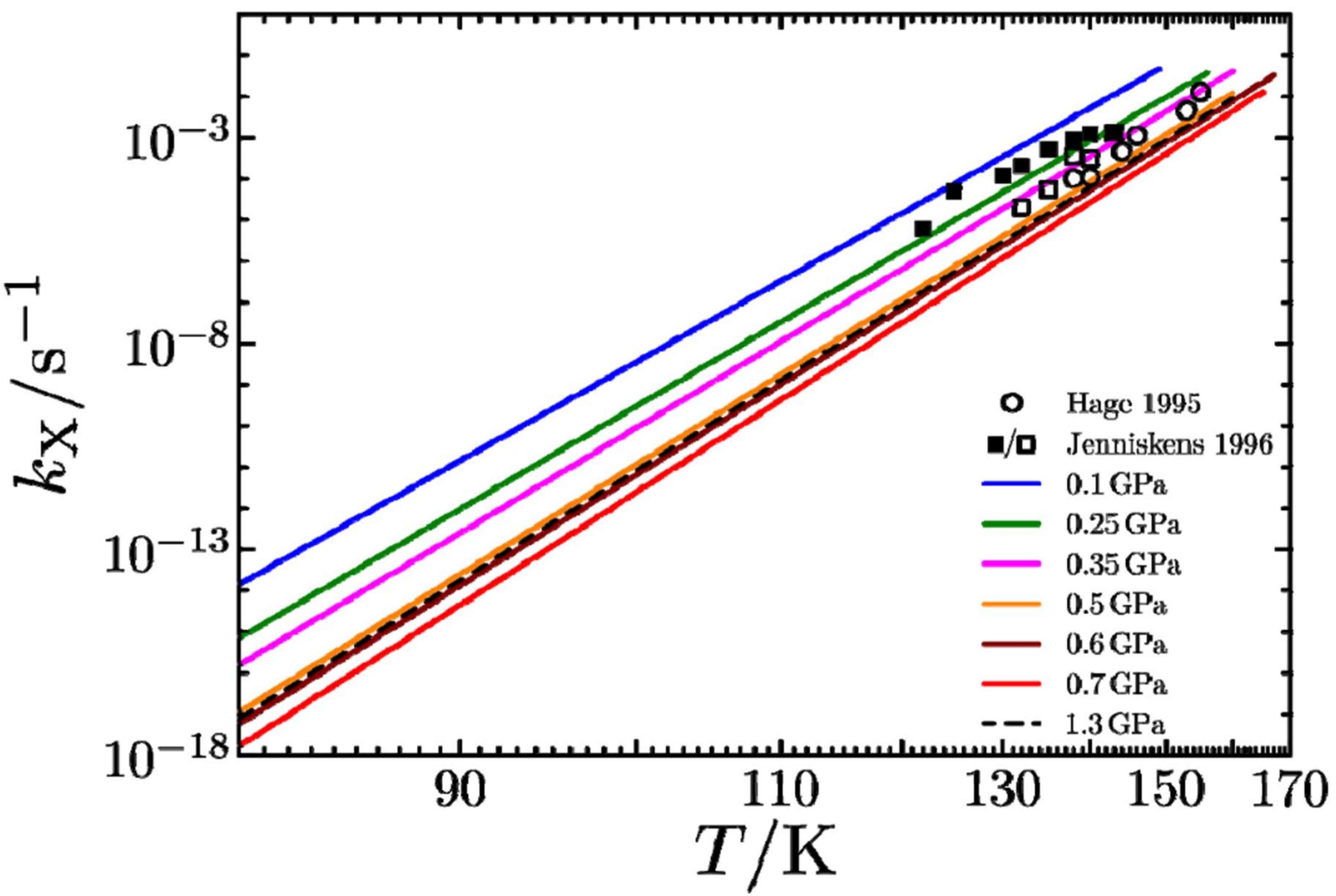
Handle, Seidl, Loerting, PRL, **108** (2012) 225901

VOLUME RELAXATION TIMES

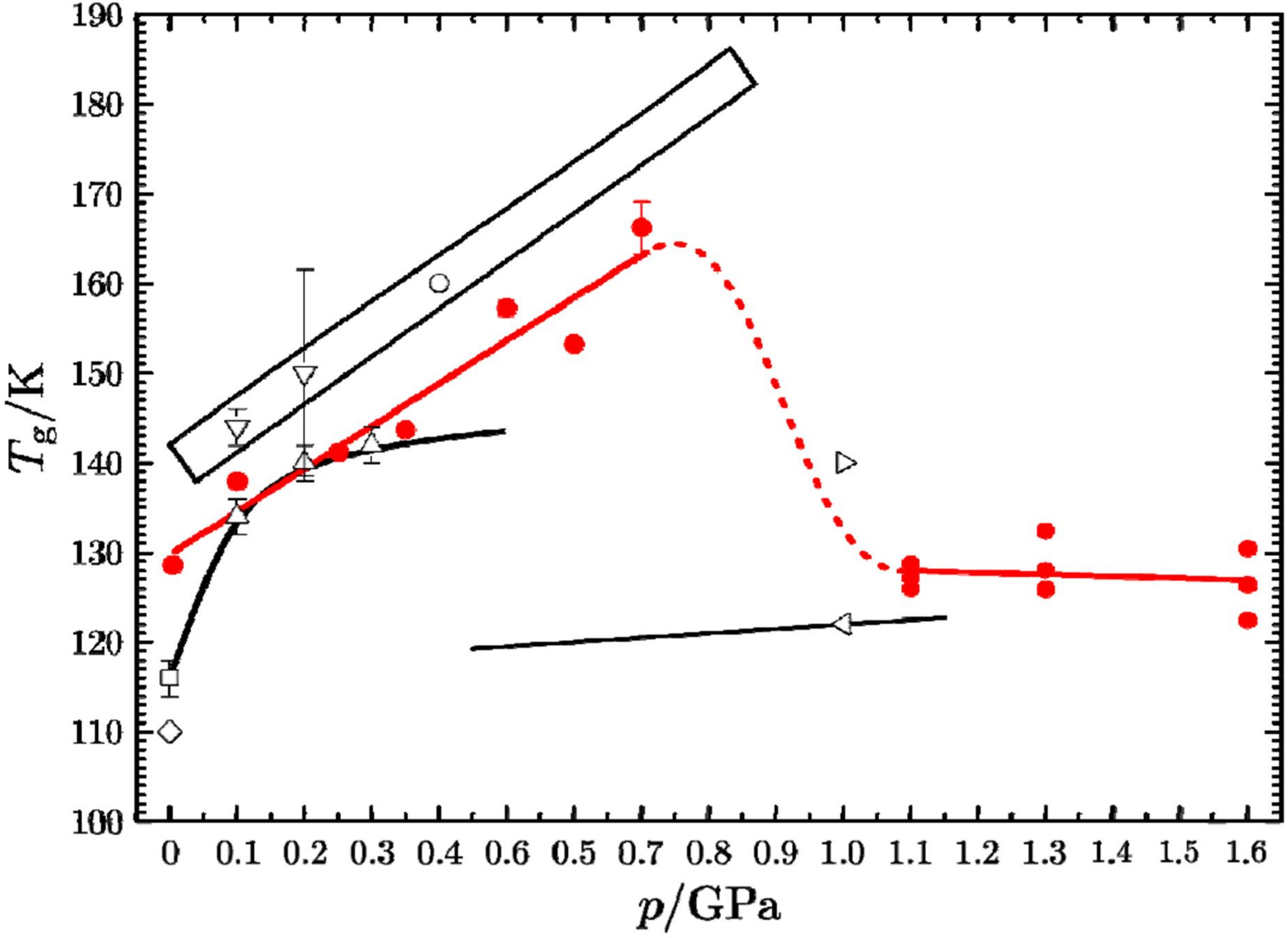
HDA - VHDA



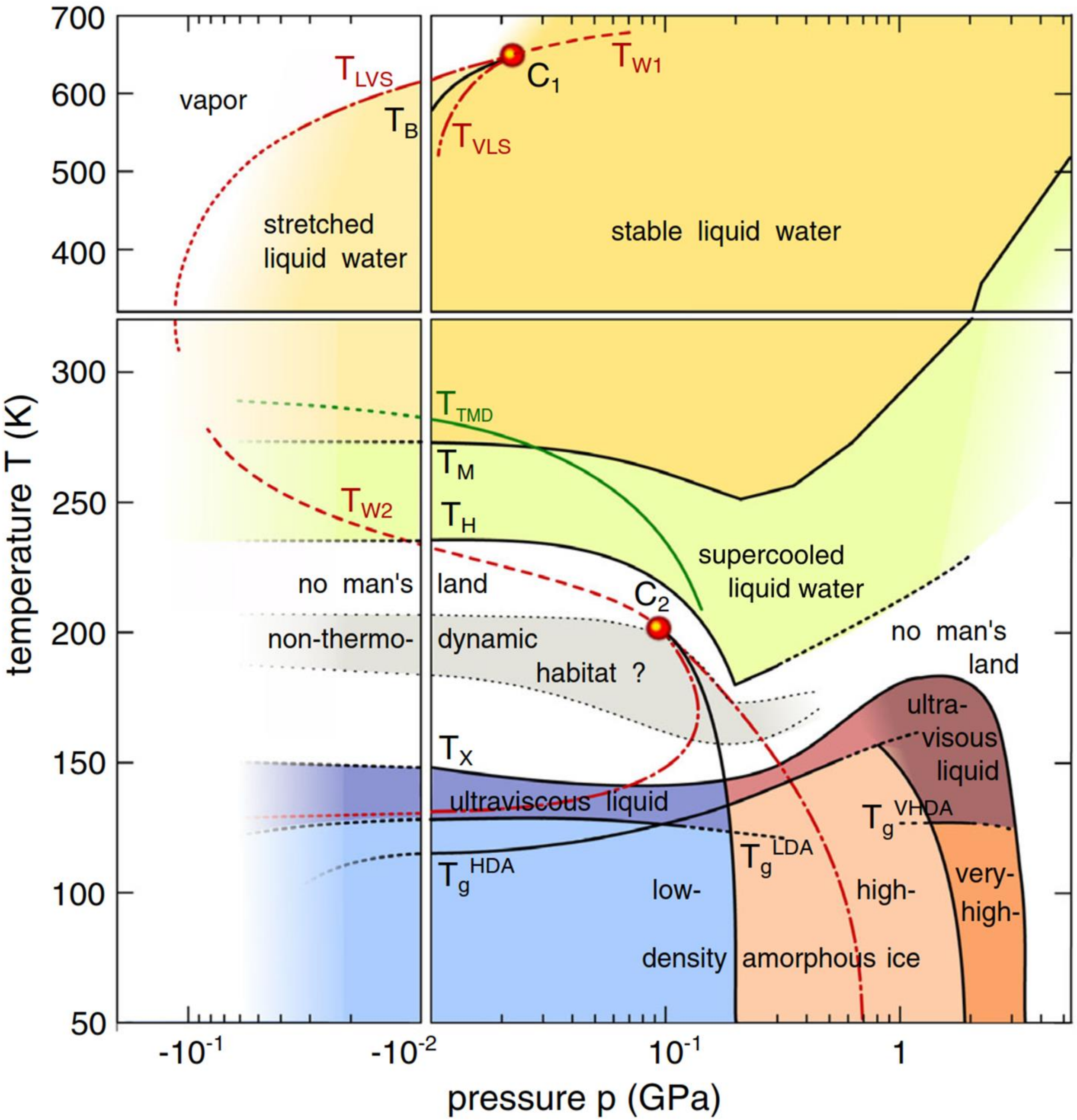
$$\Delta V_{\mathrm{m}}(t) = \sum_i \Delta_{\mathrm{e}} V_{\mathrm{m},i}\left(1 - \mathrm{e}^{-\left(\frac{\Xi_i(t)}{\mathrm{R}q\tau_{\mathrm{R},\infty,i}}\right)^{\beta_{p,i}^{V_{\mathrm{m}}}}}\right) + \propto_p^{V_{\mathrm{m}}} (T(t) - T_0).$$



k_X/s^{-1}
10^{-3}
10^{-8}
10^{-13}
10^{-18}
90
110
130
150
170
T/K
Hage 1995
Jenniskens 1996
0.1 GPa
0.25 GPa
0.35 GPa
0.5 GPa
0.6 GPa
0.7 GPa
1.3 GPa



190
180
170
160
150
140
130
120
110
100
T_g/K
0
0.1
0.2
0.3
0.4
0.6
0.5
0.7
0.8
0.9
1.0
1.1
1.2
1.3
1.4
1.5
1.6
p/GPa



Amann-Winkel et al., **Rev. Mod. Phys.** *88* (2016) 011002.


Bottom
Top
MIN MAX
HOLD
T1 T2 T1-T2
LOGGING
RECALL
SETUP
ENTER

Ehrenfest Relation

$$\frac{\Delta C_p}{TV} = \Delta\alpha \frac{dp}{dT}$$

HDA:

dTg/dp = 200 K/GPa; dp/dTg = $5 \cdot 10^{6}$ Pa/K (ambient pressure)
Δcp = 4 J/Kmol (ambient pressure)
$\Delta\alpha$ = 0.00048/K (0.1 GPa)
Tg=116 K (ambient pressure)
V = $15.7 \cdot 10^{-6}$ m^3/mol (ambient pressure)

Fulfilled (only 10% deviation!)

LDA:

dTg/dp = -20 K/GPa; dp/dTg = $-5 \cdot 10^{7}$ Pa/K (ambient pressure)
Δcp = 1 J/Kmol (ambient pressure)
$\Delta\alpha$ = 0.00008/K (0.006 GPa)
Tg=136 K (ambient pressure)
V = $19.5 \cdot 10^{-6}$ m^3/mol (ambient pressure)

Not Fulfilled (wrong sign - Delta alpha!)