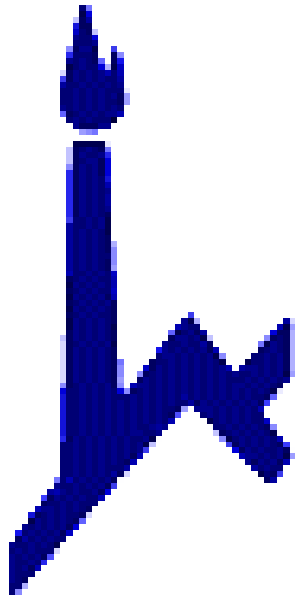


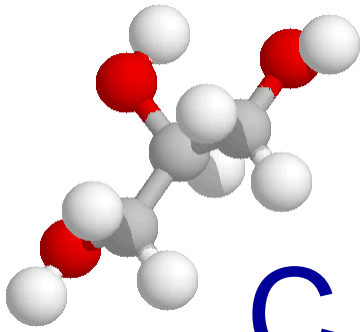
# New Features of Supercooled Glycerol Dynamics

*Ya. E. Ryabov, Y. Hayashi, A. Gutina & Yu. Feldman*



The Hebrew University of Jerusalem,  
Graduate School of Applied Science,  
Department of Applied Physics  
Givat Ram, 91904, Jerusalem, Israel





# Glycerol

Glass Transition

$$T_G = 190 \text{ K}$$

Melting point

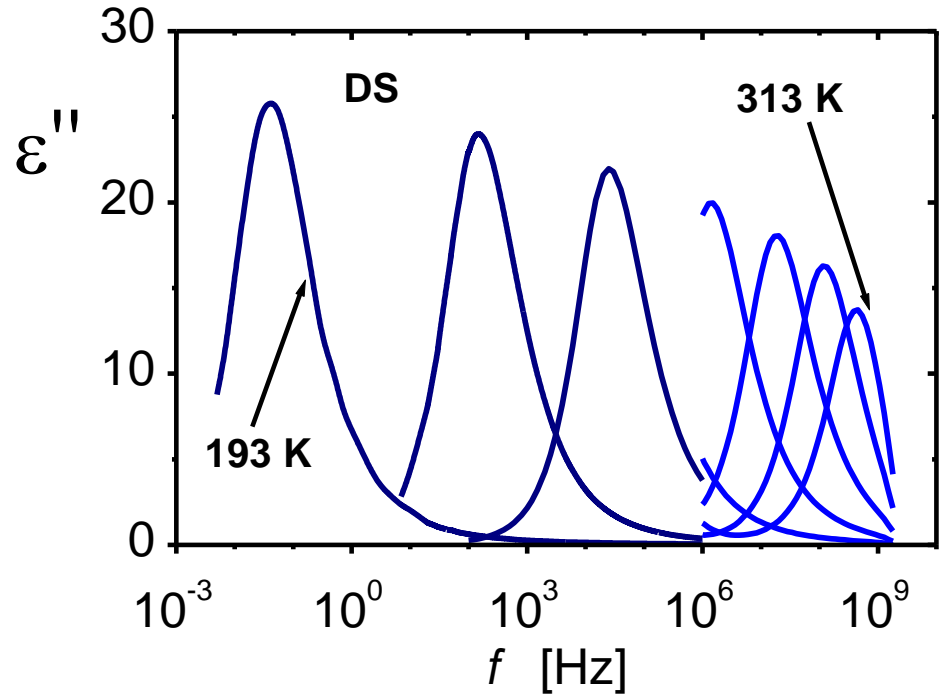
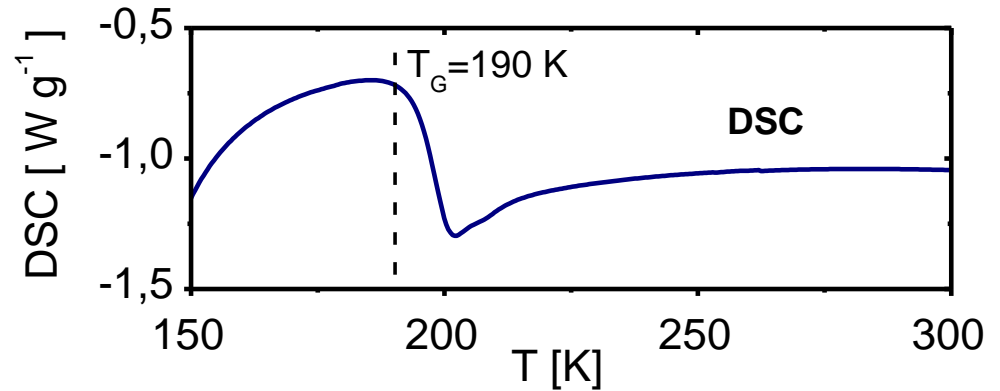
$$T_m = 293 \text{ K}$$

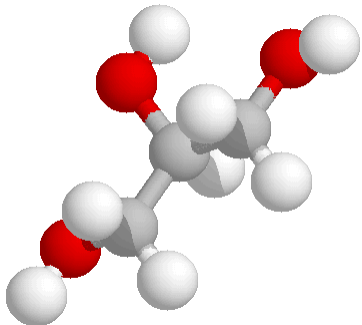
Specific gravity

1.261

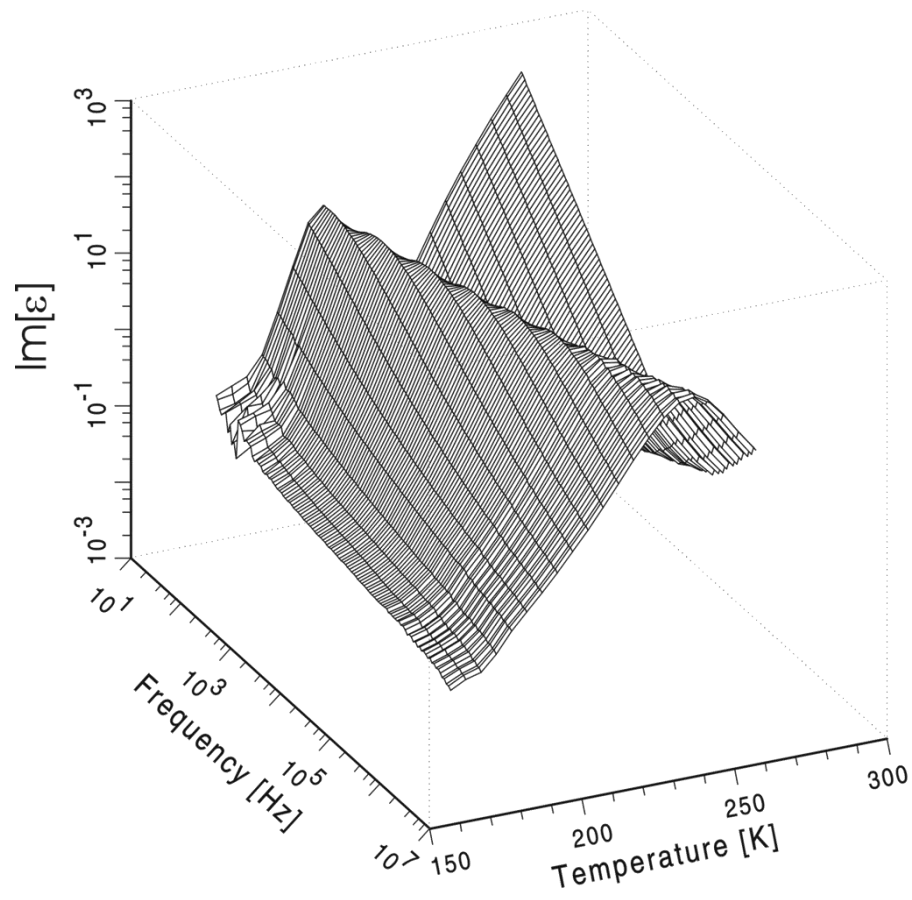
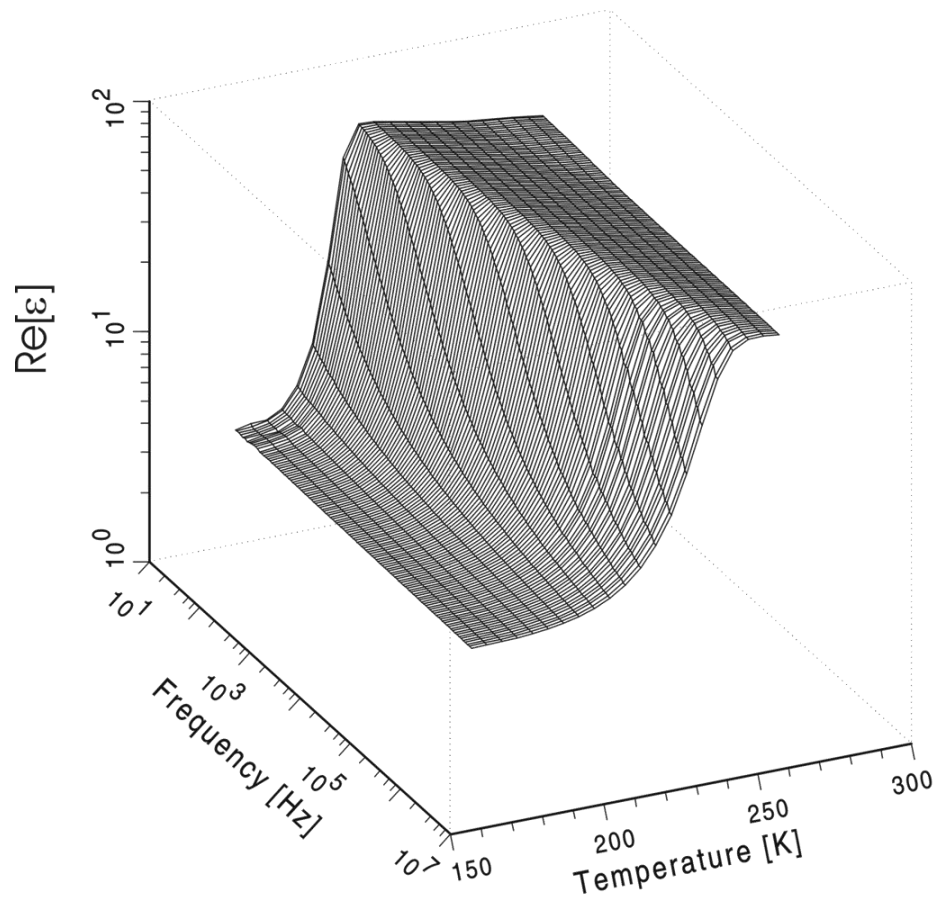
Molecular weight

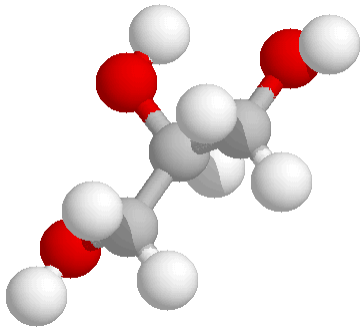
92.1





# DS of Glycerol

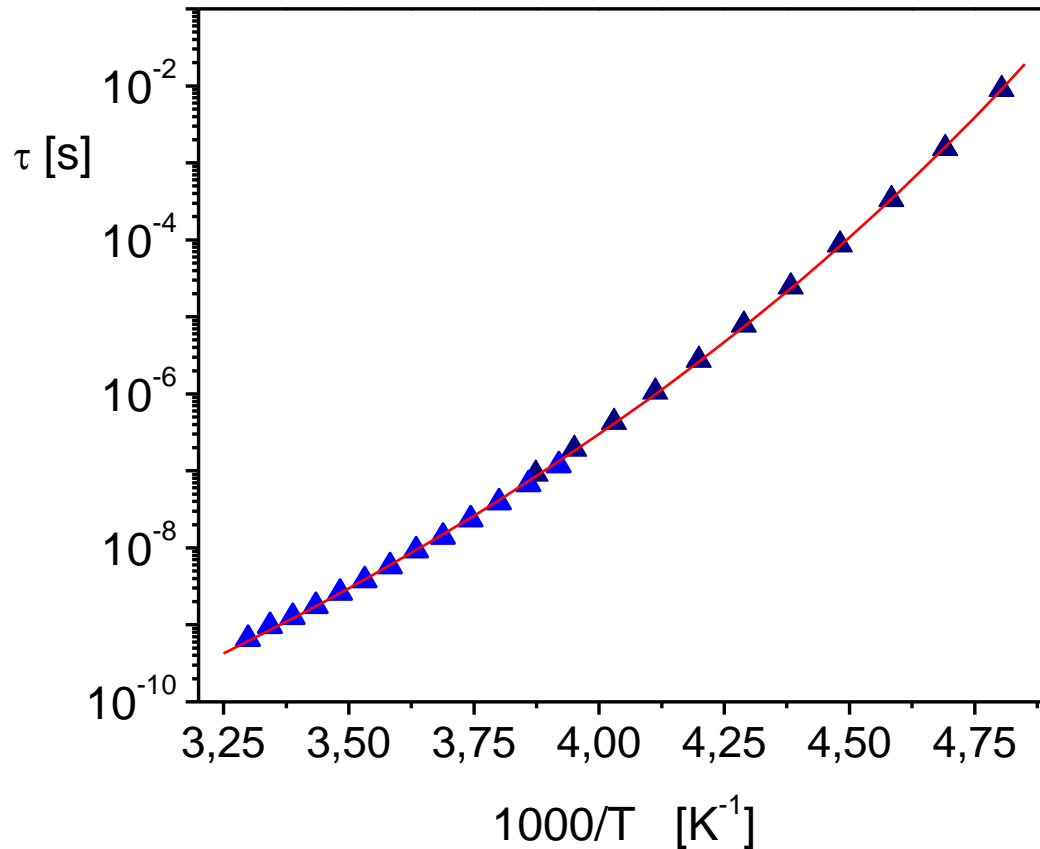




# DS of Glycerol

## Vogel Fulcher Tammann

$$\tau = \tau_v \text{Exp}(D T_v / (T - T_v))$$

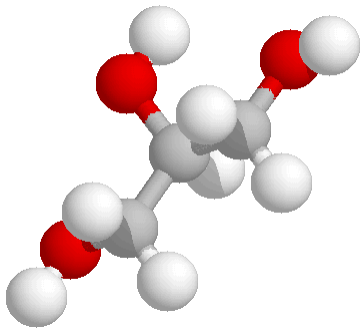


$$T_v = 122.9 \pm 1.7 \text{ K}$$

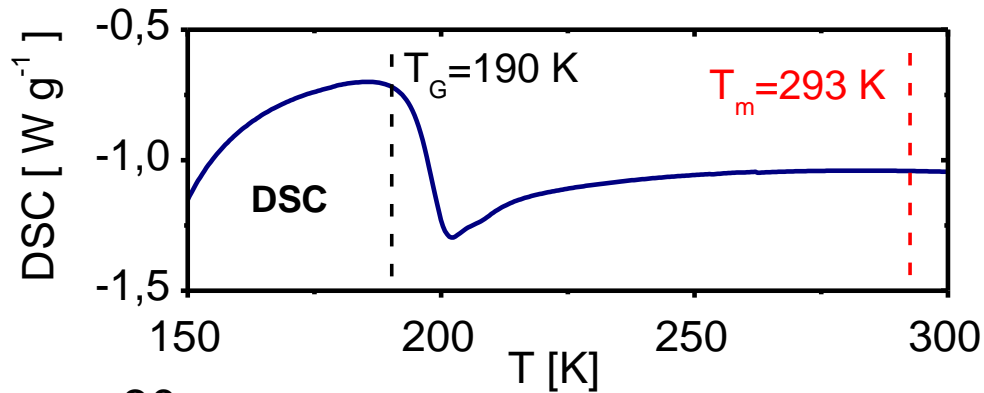
$$\tau_v = 2.2 \cdot 10^{-16} \pm 0.7 \cdot 10^{-16} \text{ s}$$

Fragility

$$D = 21.7 \pm 0.3$$

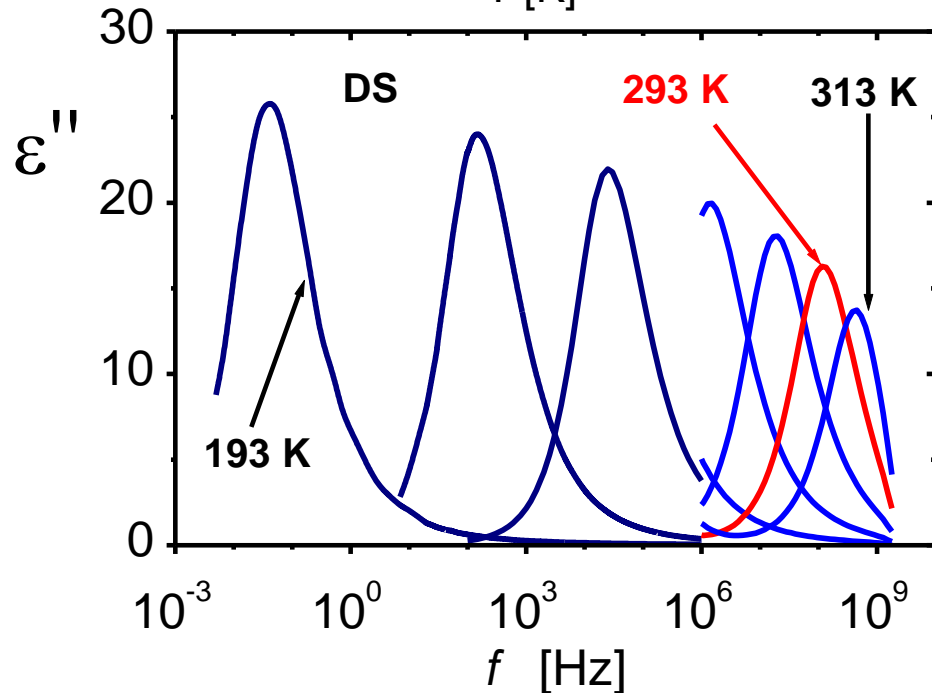


# Glycerol Crystallization

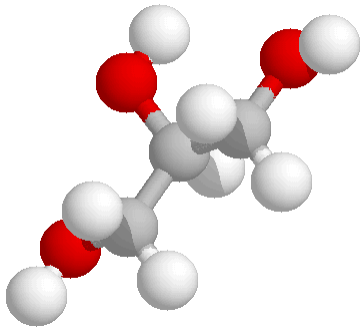


Melting point

$T_m = 293 \text{ K}$

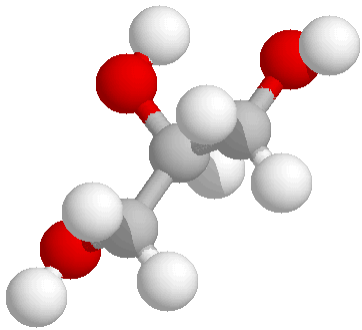


What is  
the crystallized  
Glycerol ?



# Objectives for our study

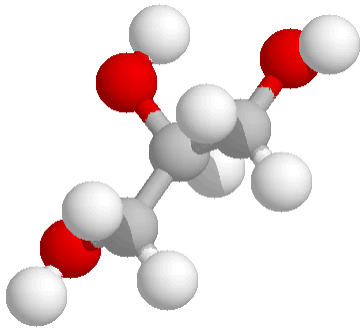
- **To investigate Glycerol crystallization by Dielectric Spectroscopy technique**
- **To find out if any special features of Glycerol near the crystallization region**
- **What new information about Glycerol glass-forming dynamics we can gain from this study ?**



# How to crystallize Glycerol ?

- One need to use pure dehydrated Glycerol
- Cool it down below the  $T_G$
- Hold it at this temperature for several hours
- Heat it up to the temperature slightly below the  $T_m$
- Hold it for crystallization

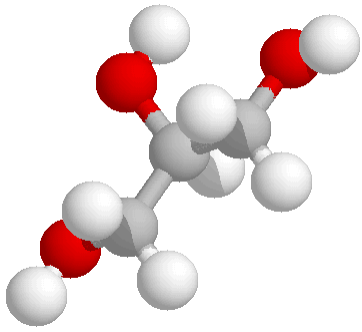
X-Ray study by Van Koningsveld, H. *Rec. Trav. Chim.* 87, 243-254 (1968)



# Experimental Procedure

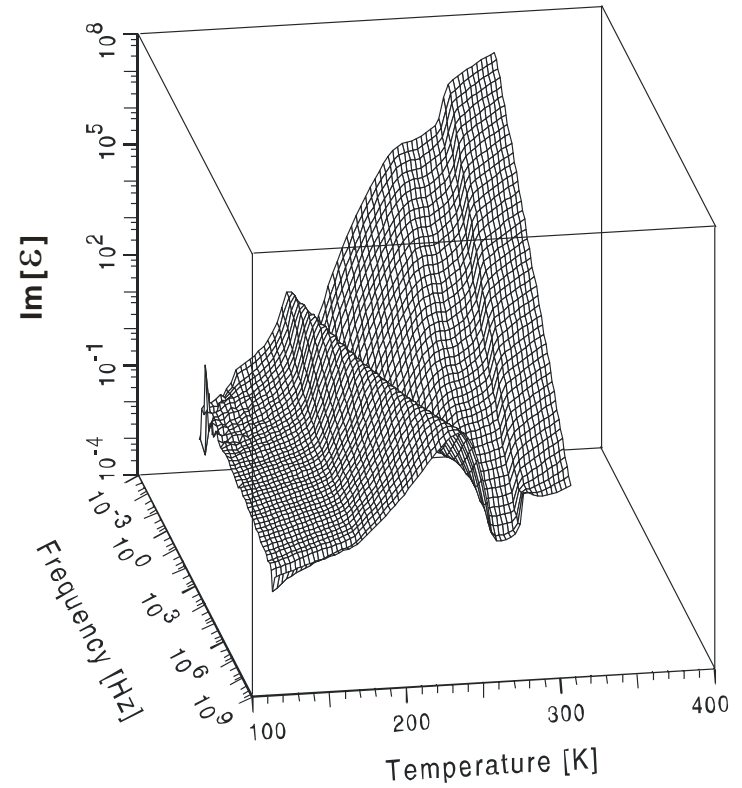
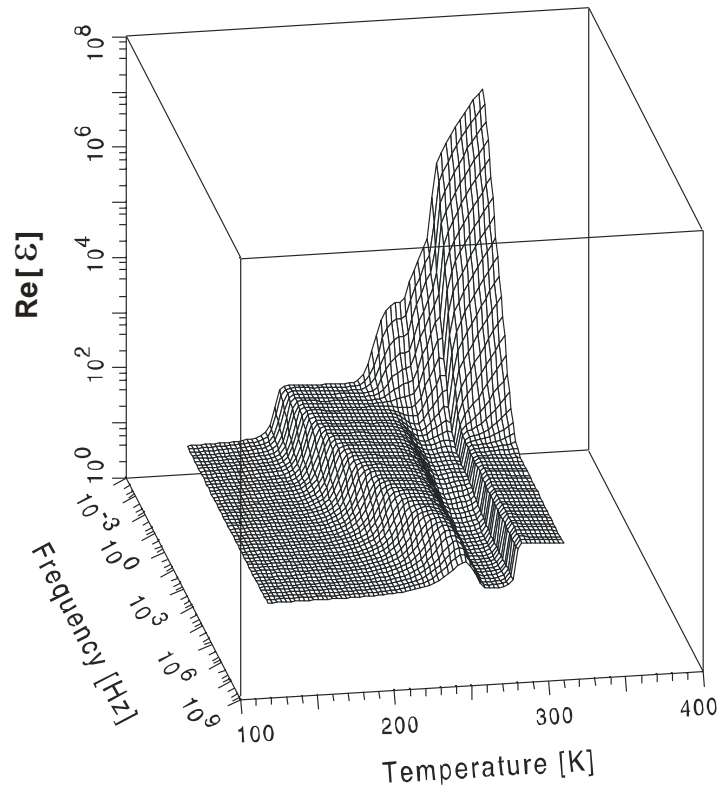
- We used pure dehydrated Glycerol from Sigma
- Cool it down to 140 K
- Novocontrol BDS 80 used to measure dielectric permittivity while heating in the temperature interval  
140K ÷ 313 K with the step of 3 K  
and frequency band  
0.01 Hz ÷ 3 MHz
- Thus each temperature point takes about 20 min to measure and overall experiment time was about 30 hours

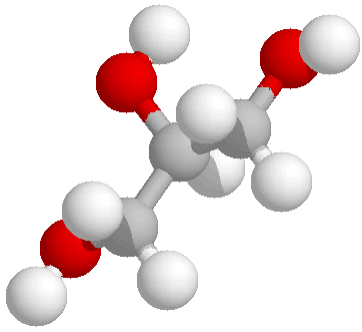




# DS Experimental Findings

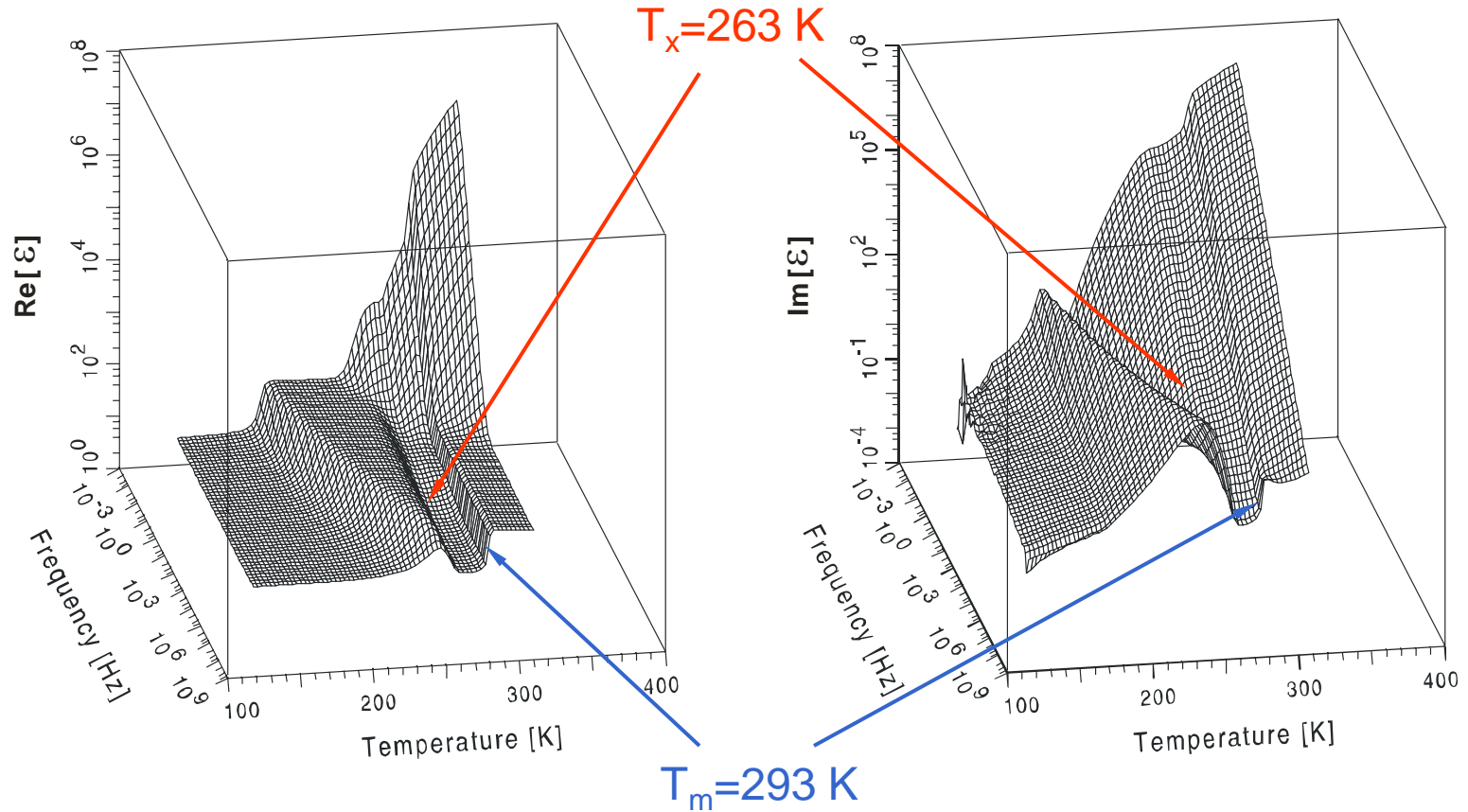
Pure dehydrated Glycerol  
measured while heating

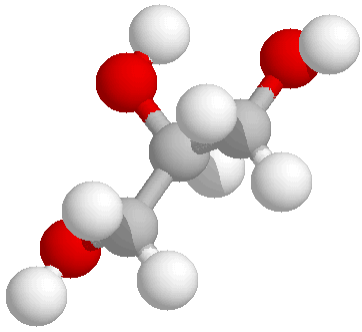




# DS Experimental Findings

Pure dehydrated Glycerol  
measured while heating

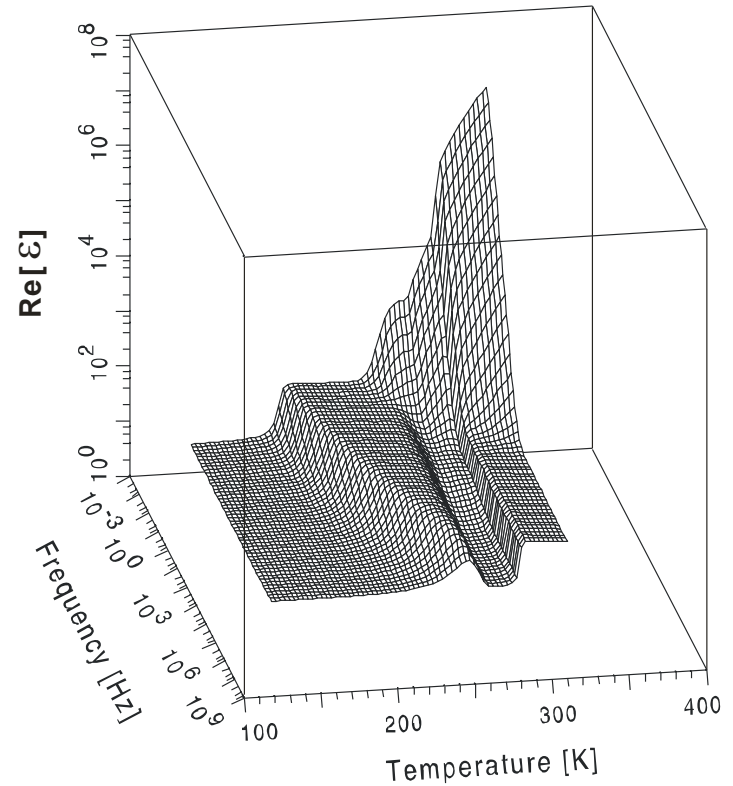
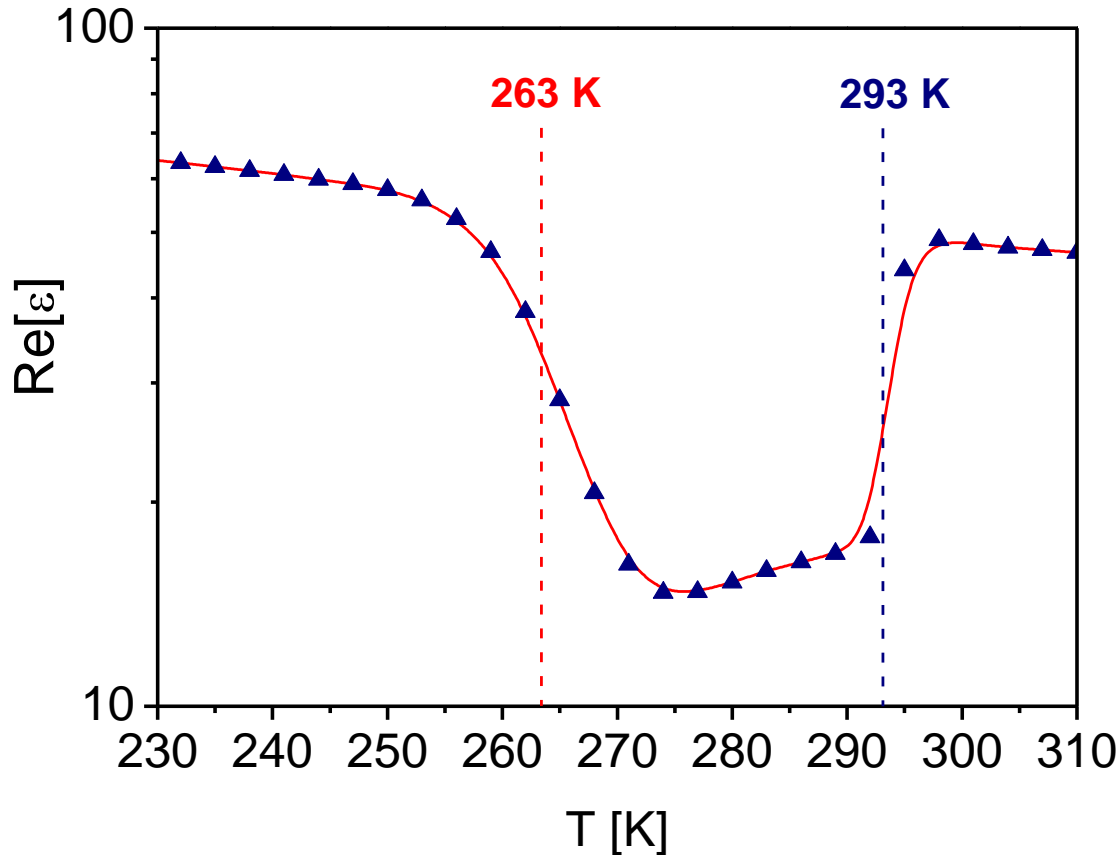


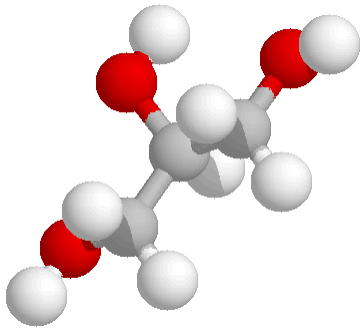


# DS Experimental Findings

Pure dehydrated Glycerol  
measured while heating

$f = 95.2 \text{ Hz}$

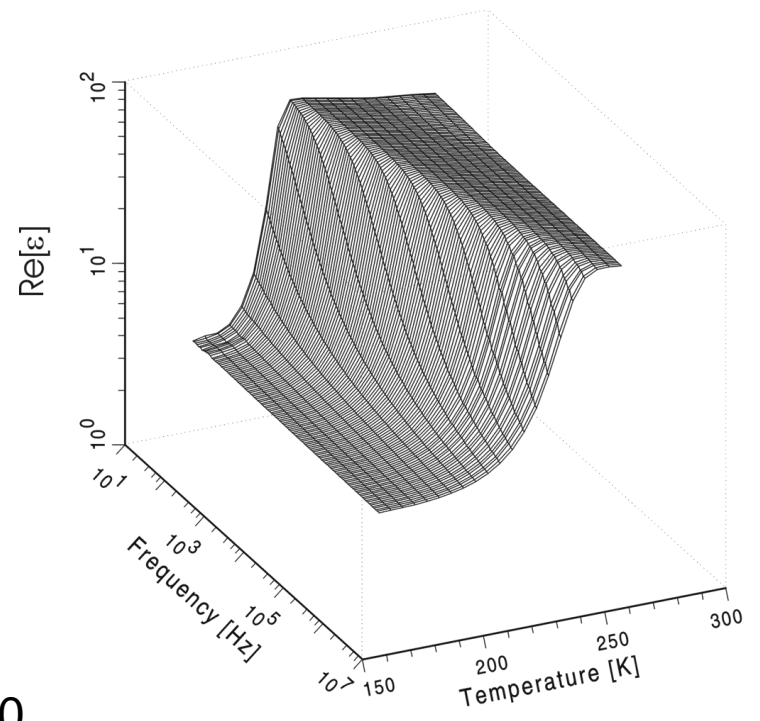
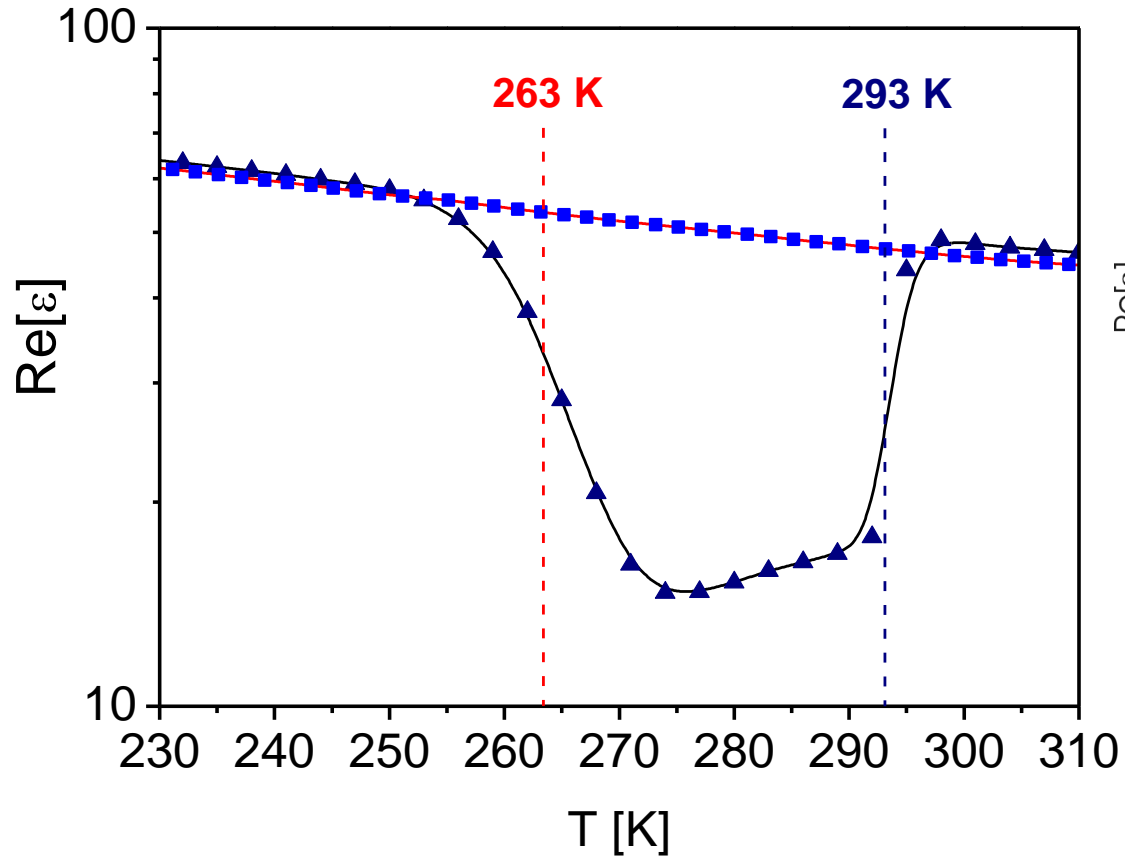


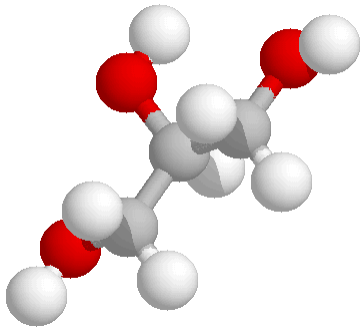


# DS Experimental Findings

**NOT** dehydrated Glycerol  
measured while heating in **reduced temperature interval**

$f = 95.2 \text{ Hz}$

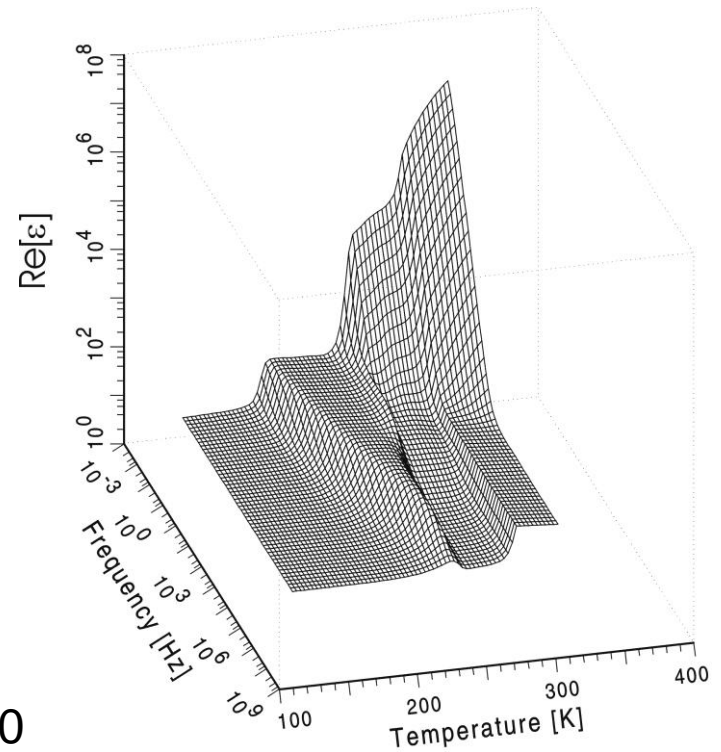
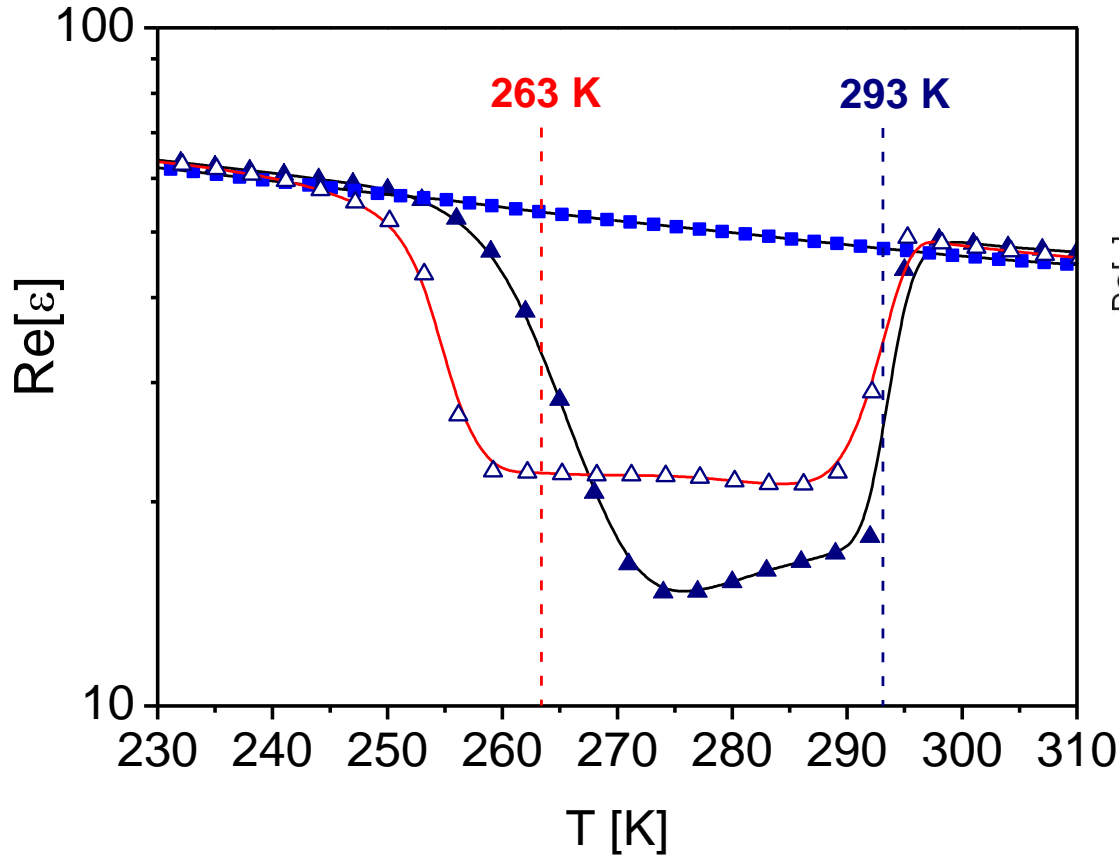


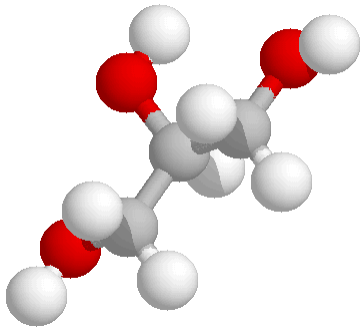


# DS Experimental Findings

**NOT** dehydrated Glycerol  
measured while heating in **WHOLE** temperature interval

$f = 95.2 \text{ Hz}$

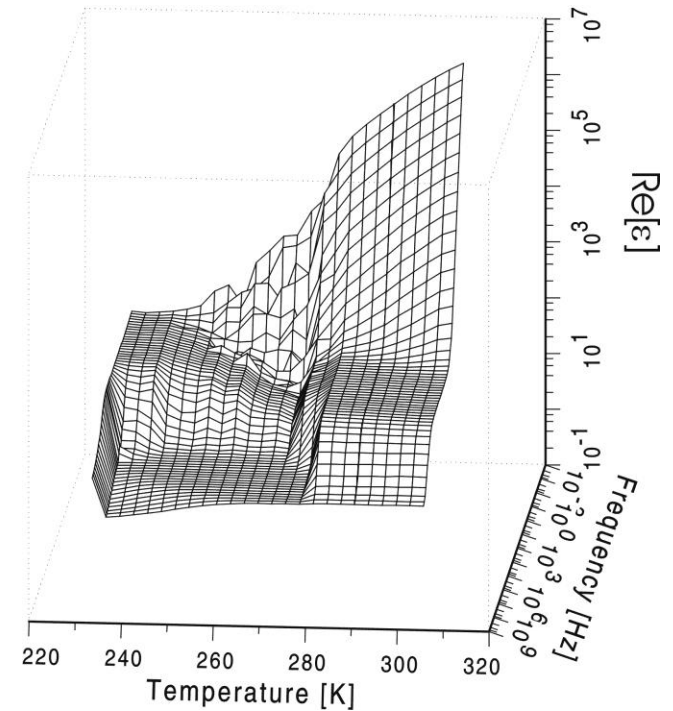
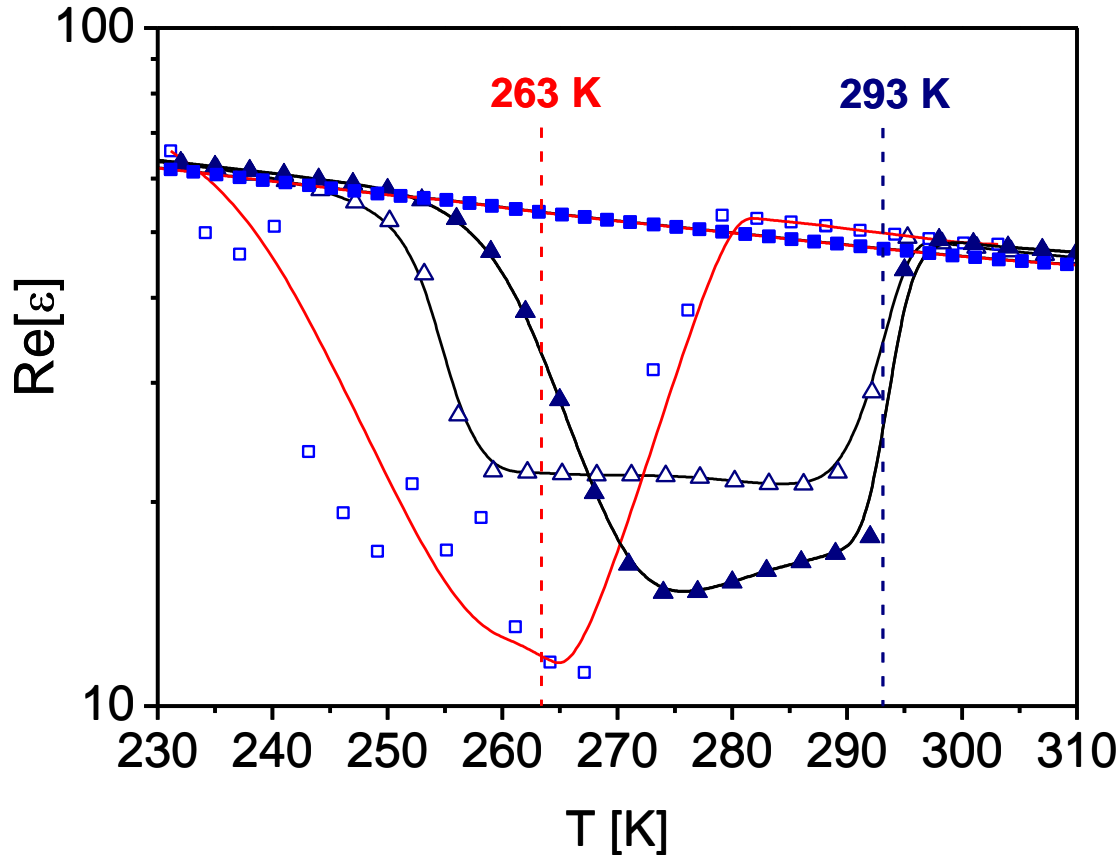


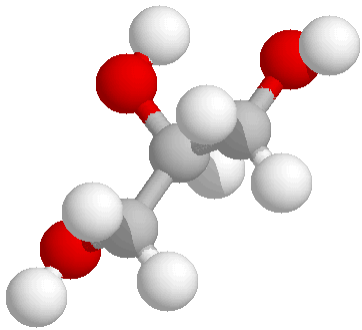


# DS Experimental Findings

Pure dehydrated Glycerol  
measured while cooling

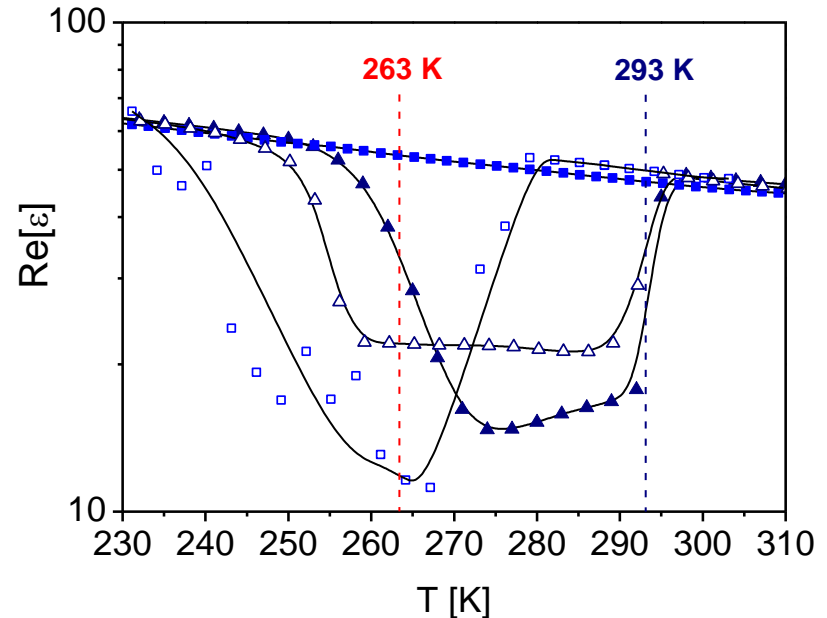
$f = 95.2 \text{ Hz}$

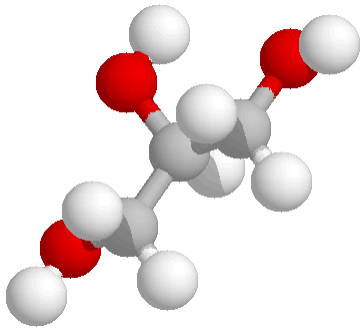




# Experimental Findings

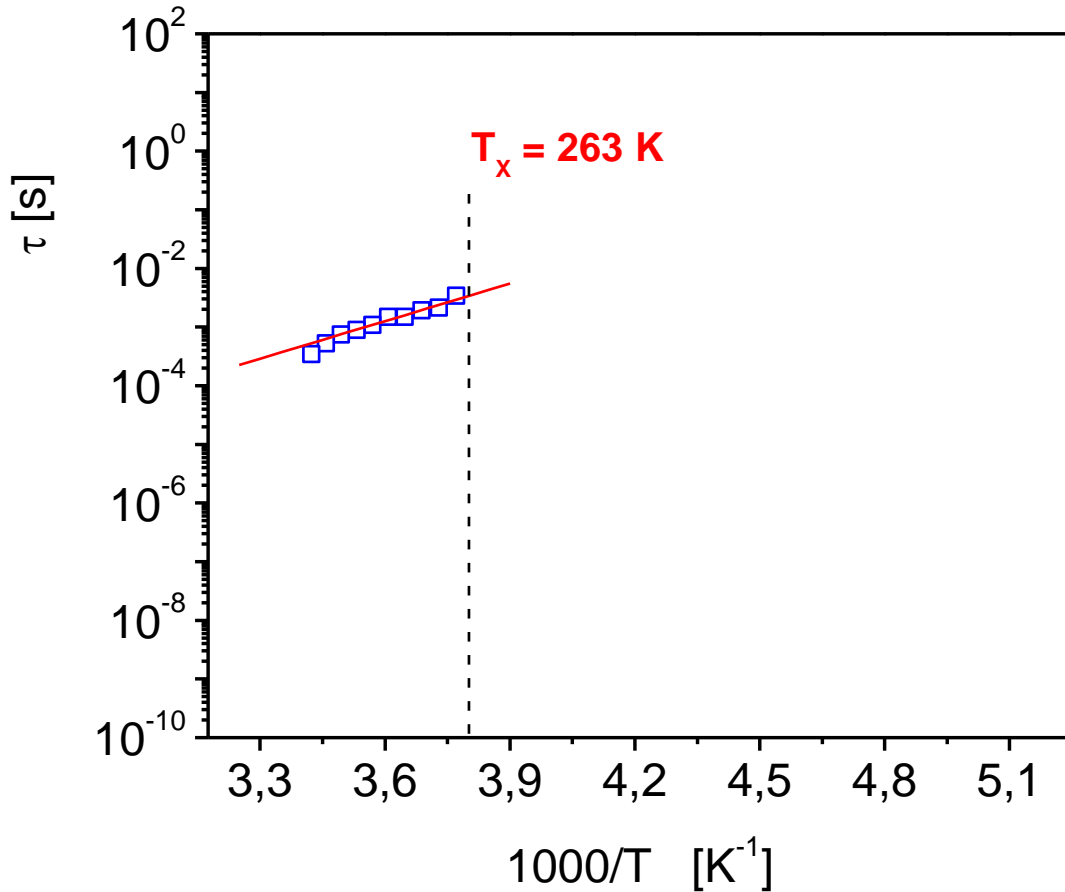
- In usual condition Glycerol can not be crystallized
- Pure Dehydrated Glycerol could be crystallized while heating at **263 K**
- Crystallization of glycerol while cooling is very unstable. Moreover cooling below the 263K plasticizes Glycerol, which undergoes in the state of a supercooled liquid
- Crystallization and Relaxation Dynamics of Glycerol dependent on the Thermal History and impurities





# Relaxation of crystallized and supercooled Glycerol

## Crystallized Glycerol



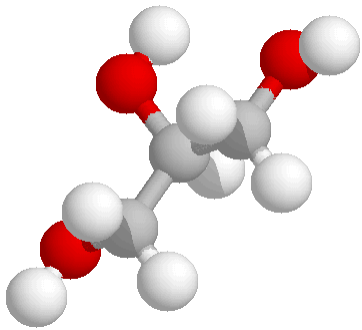
Arrhenius law

$$\tau = \tau_0 \text{Exp} (E_A / k T)$$

$$E_A = 41 \pm 6 \text{ kJ mol}^{-1}$$

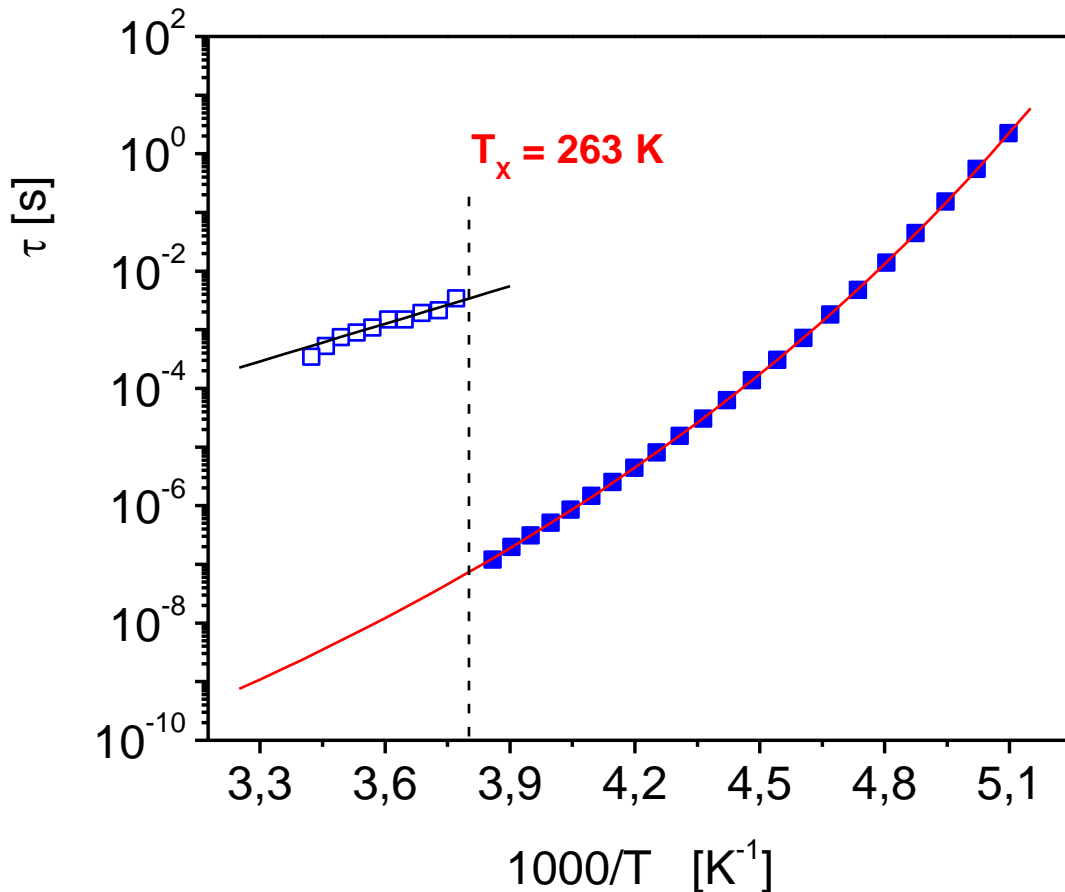
$$\tau_0 = 2.7 \cdot 10^{-11} \pm 1 \cdot 10^{-11} \text{ s}$$





# Relaxation of crystallized and supercooled Glycerol

Pure dehydrated supercolled Glycerol



Vogel Fulcher Tammann

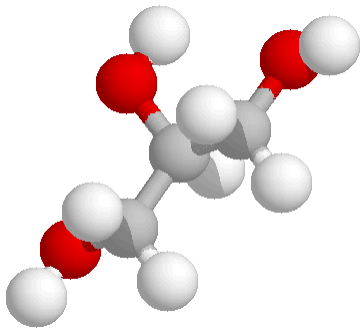
$$\tau = \tau_v \text{Exp} (D T_v / (T - T_v))$$

$$T_v = 122.1 \pm 0.5 \text{ K}$$

$$\tau_v = 3.9 \cdot 10^{-16} \pm 0.6 \cdot 10^{-16} \text{ s}$$

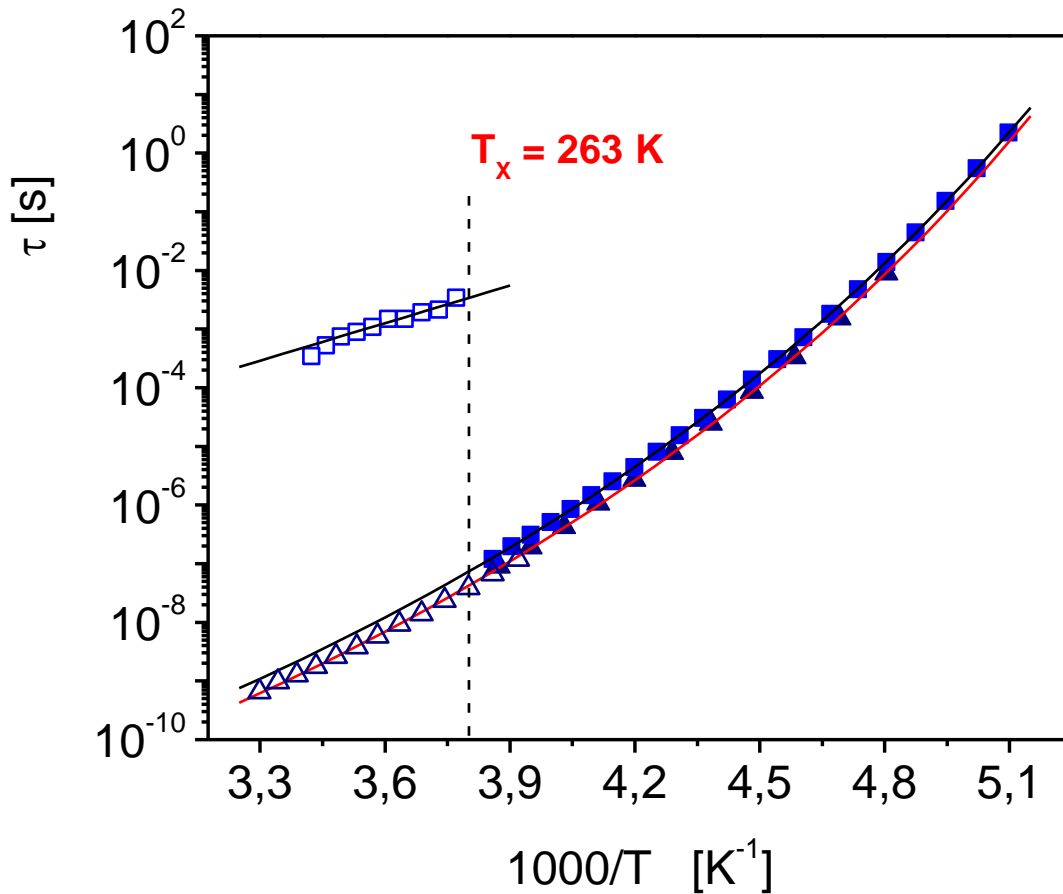
Fragility

$$D = 21.9 \pm 0.3$$



# Two relaxation patterns of supercooled Glycerol

USUAL supercooled Glycerol



Vogel Fulcher Tammann

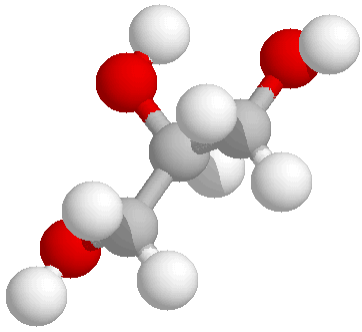
$$\tau = \tau_v \text{Exp} (D T_v / (T - T_v))$$

$$T_v = 122.9 \pm 1.7 \text{ K}$$

$$\tau_v = 2.2 \cdot 10^{-16} \pm 0.7 \cdot 10^{-16} \text{ s}$$

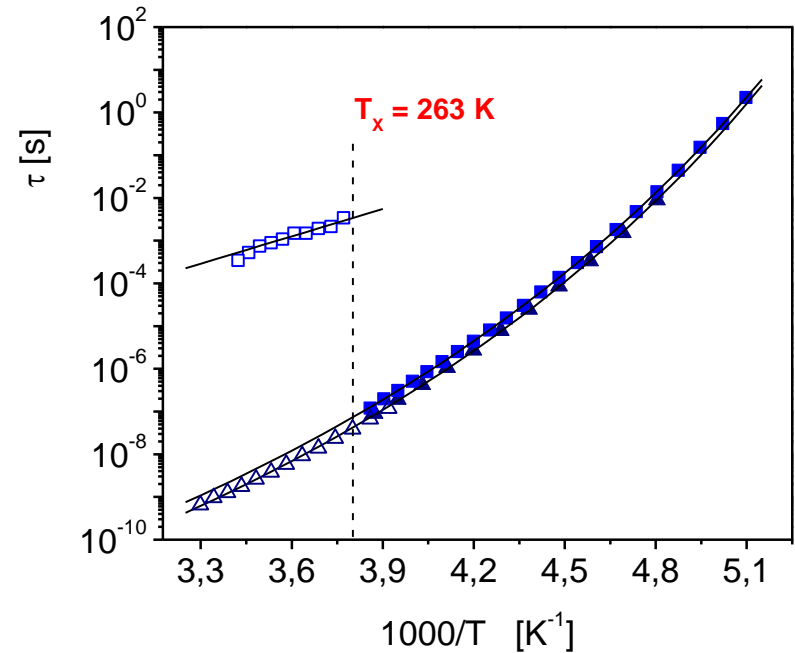
Fragility

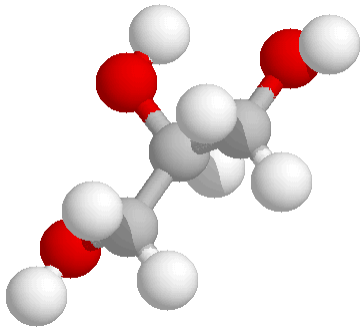
$$D = 21.9 \pm 0.3$$



# Two relaxation patterns of supercooled Glycerol

- Relaxation time correspondent to the dehydrated sample is about 40% bigger than relaxation time for usual glycerol behaviour. This observation signifies that even in the supercooled liquid phase before the crystallization glycerol could follow two different dynamical patterns





# Kirkwood Correlation factor

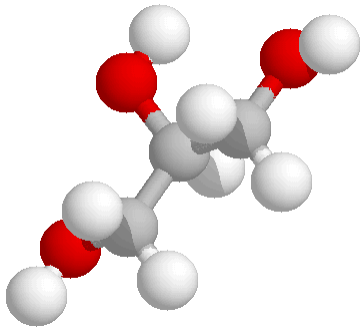
$$g = \frac{9\epsilon_0 M kT (\epsilon_s - \epsilon_\infty)(2\epsilon_s + \epsilon_\infty)}{\rho N_a \mu^2 \epsilon_s (\epsilon_\infty + 2)^2}$$

$$g = 1 + z \langle \cos \theta_{ij} \rangle$$

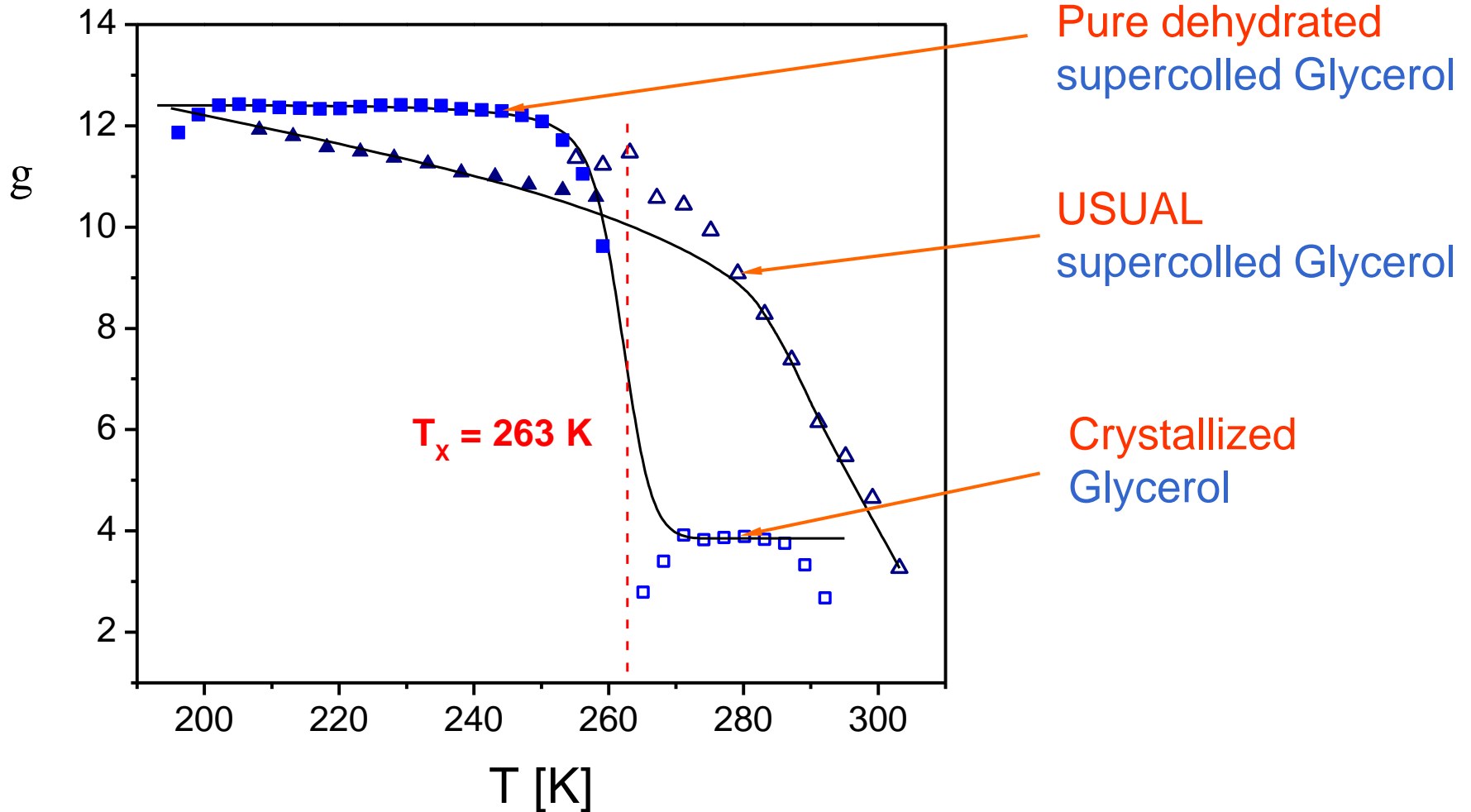
$g > 1$  signifies that the neighboring dipoles have tendency to the parallel orientation

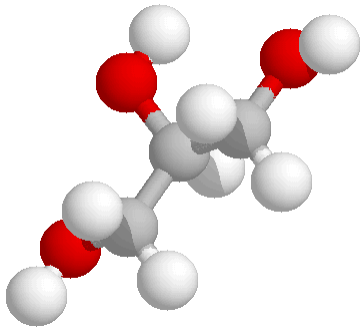
$0 < g < 1$  means anti parallel orientation

$g = 1$  corresponds to the random dipole orientation



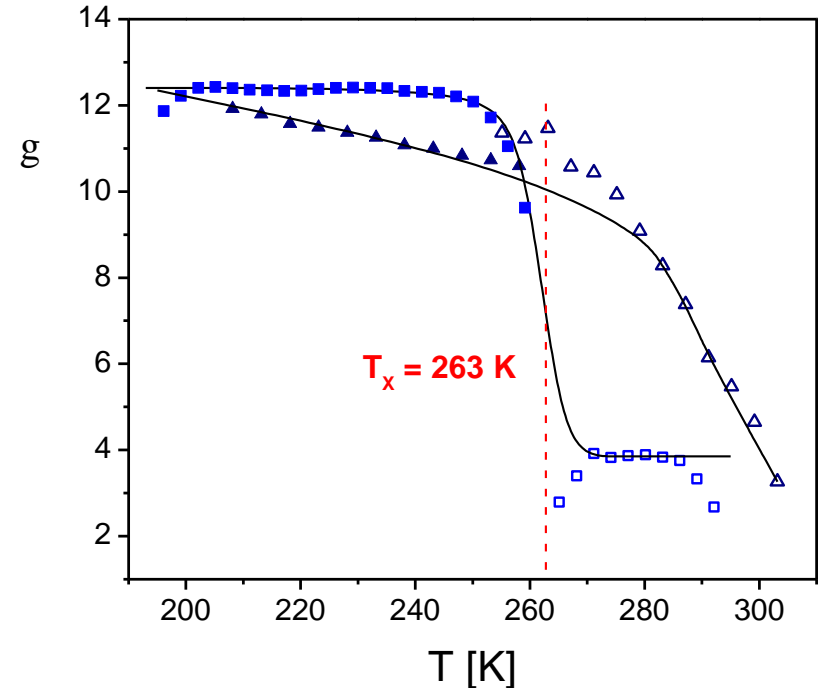
# Kirkwood Correlation factor

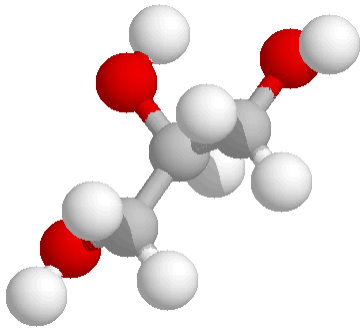




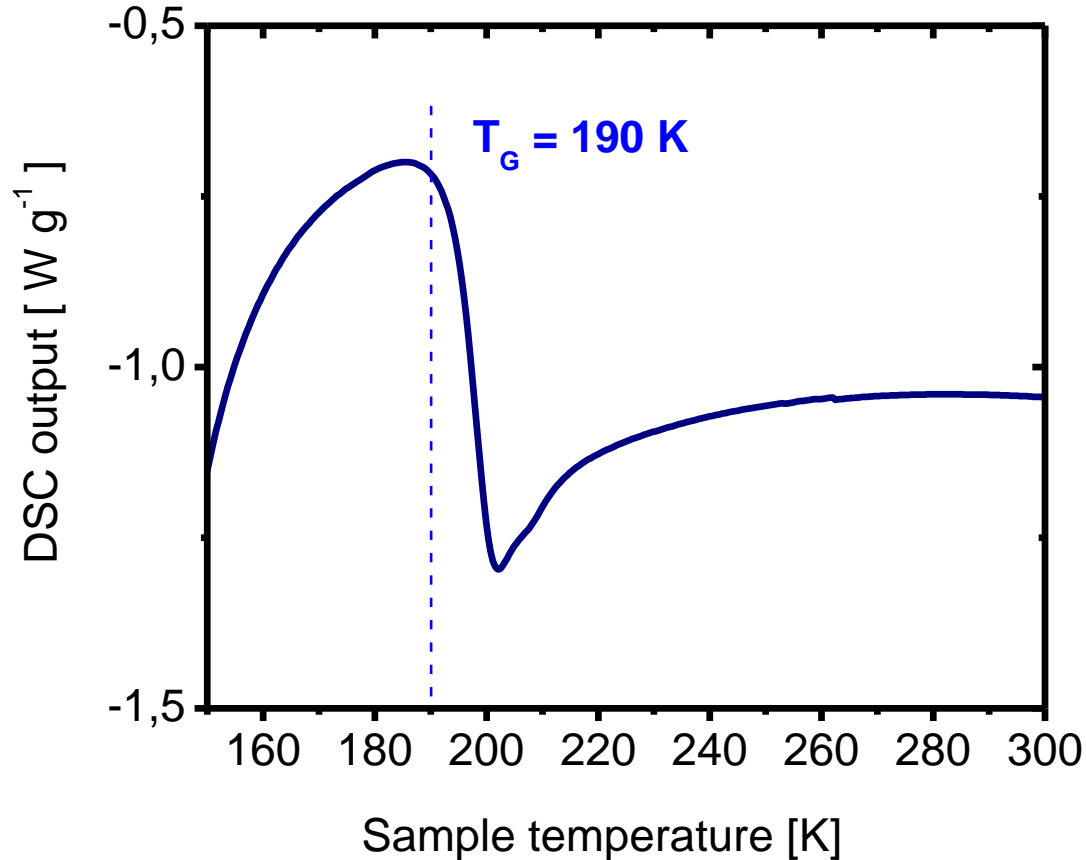
# Kirkwood Correlation factor

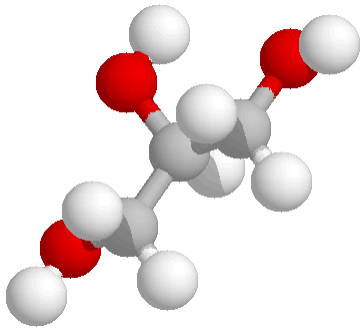
- For super-cooled liquid phase of dehydrated glycerol before the crystallization the temperature dependence of parameter  $g$  is almost negligible while for the usual glycerol behavior without crystallization the strong temperature dependence is observed.
- Thus, two different dynamical patterns of glycerol behavior are related to two different structural organization of the glycerol in supercooled liquid phase.



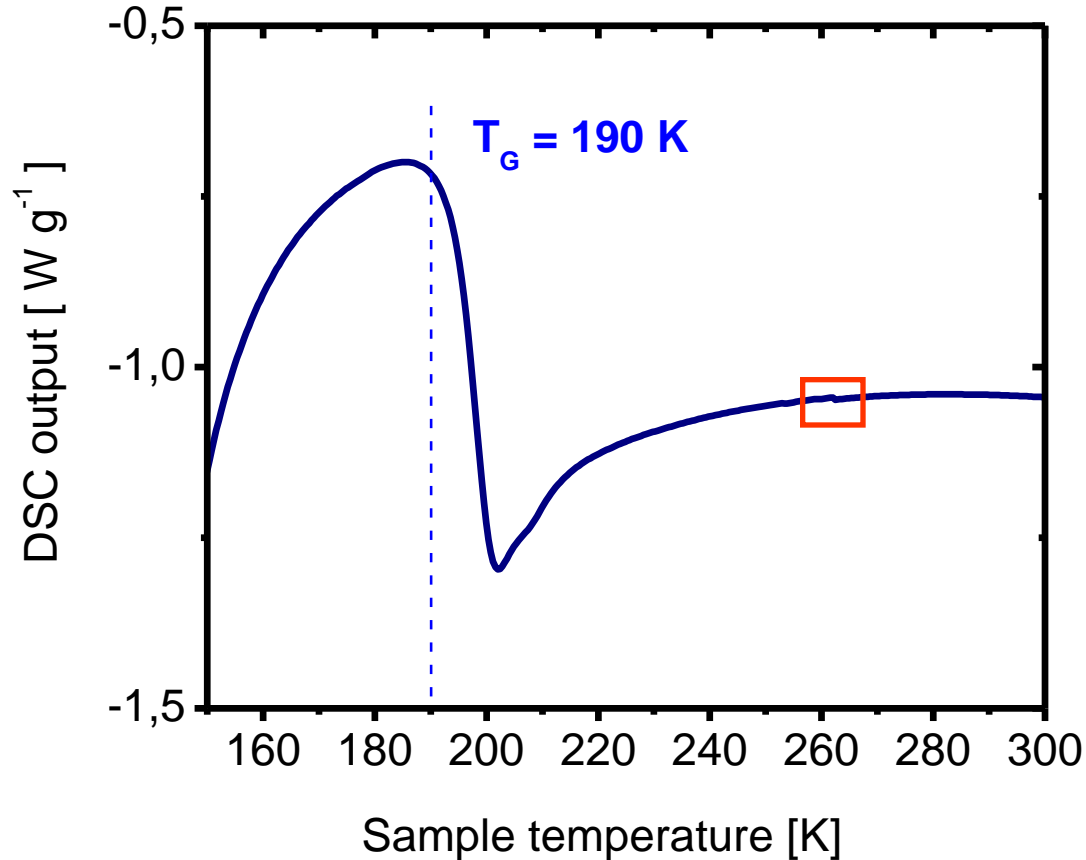


# DSC of **Pure** Dehydrated supercooled Glycerol

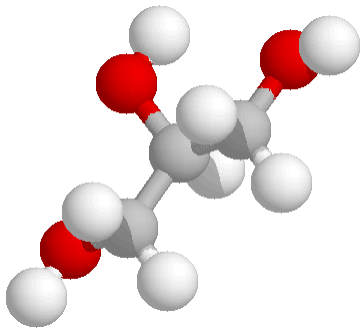




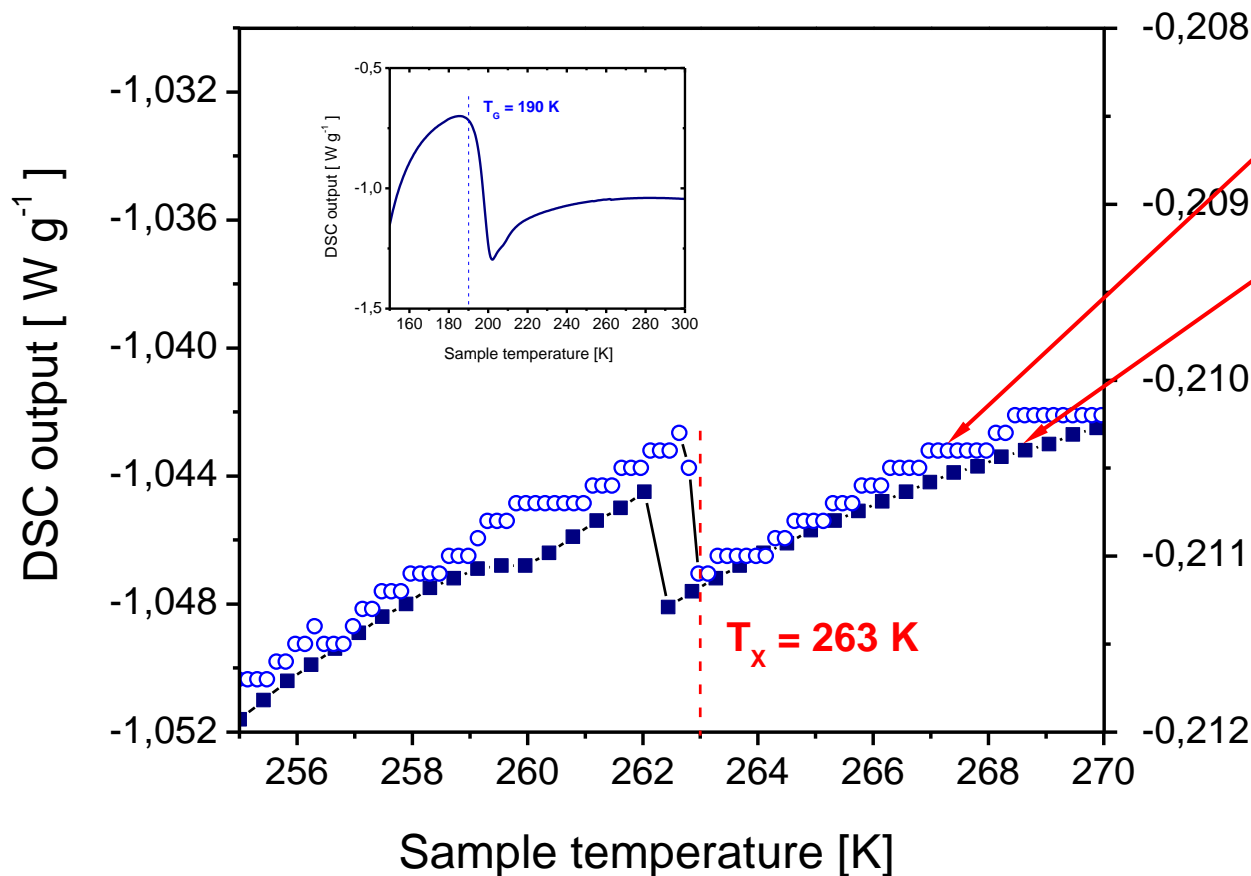
# DSC of **Pure** Dehydrated supercooled Glycerol







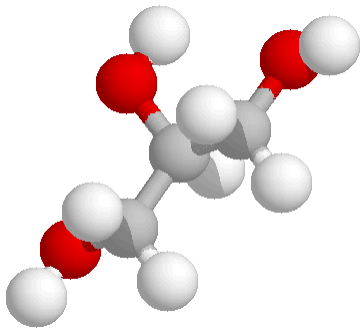
# DSC of **Pure** Dehydrated supercooled Glycerol



5 K / min

25 K / min

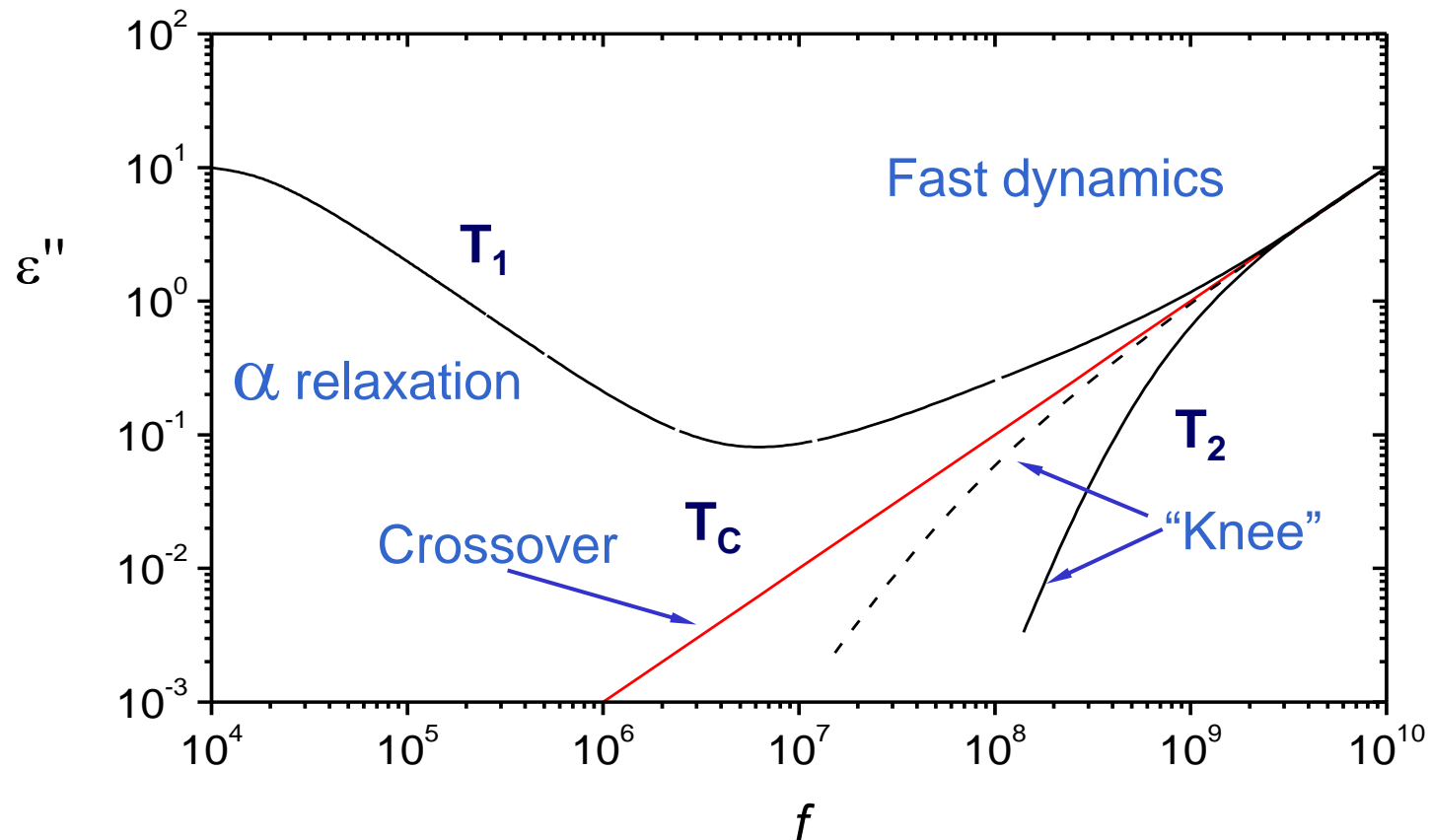
- The change of DSC output observed for glycerol at 263 K amounts 0.5% of the DSC output change in glass transition.



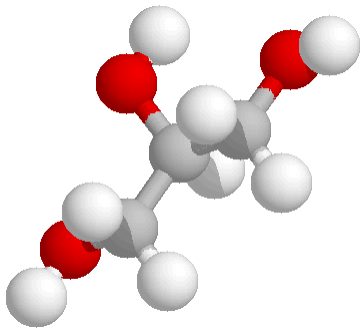
# Discussion

## MCT and its problem in the case of Glycerol

$$T_1 > T_c > T_2$$



Götze, W., Sjögren, L. *Rep. Prog. Phys.* 55, 241-376 (1992).

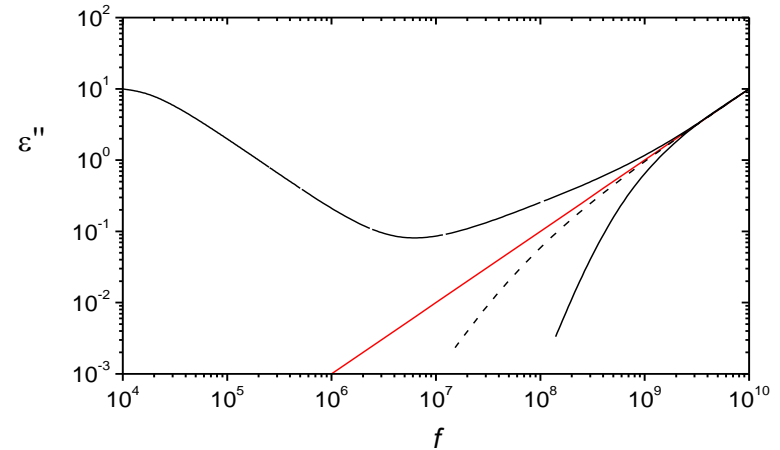


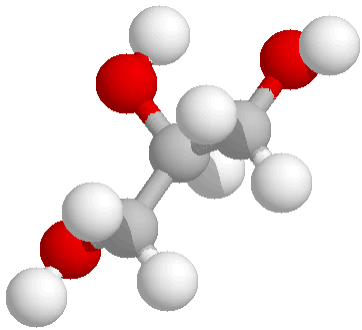
# Discussion

## MCT and its problem in the case of Glycerol

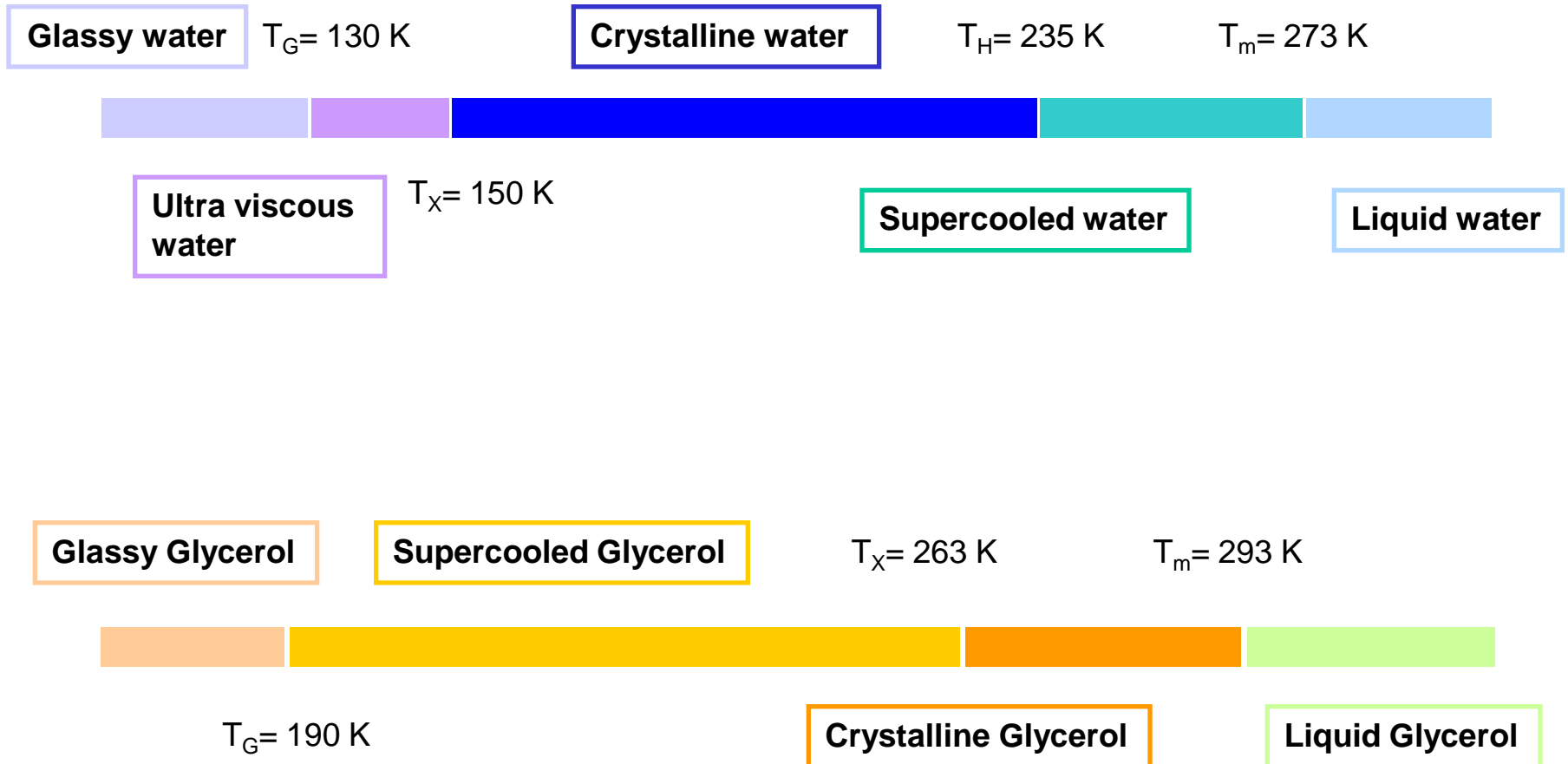
$$1.24 T_G < T_C < 1.6 T_G$$

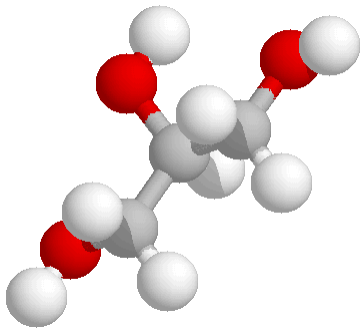
- **Dynamical crossover should be accompanied by non monotonic behavior of Heat Capacity**
- **Usual** Supercooled Glycerol does not show “knee” predicted by MCT and does not exhibit non monotonic behavior of Heat Capacity in expected temperature region



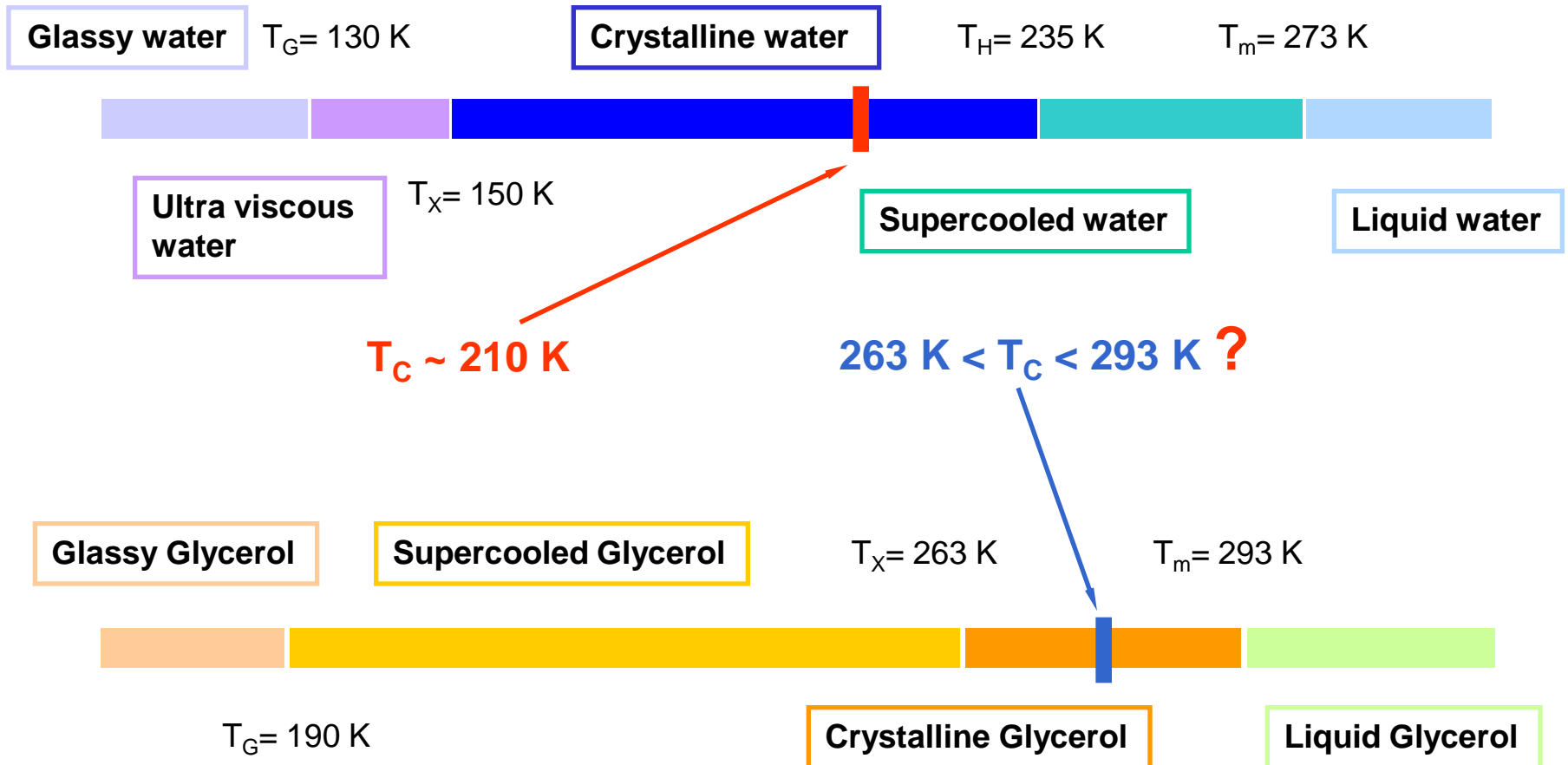


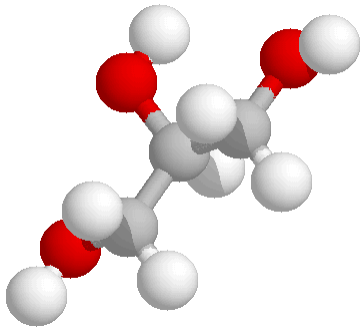
# Comparison with Hyper-Quenched Water





# Comparison with Hyper-Quenched Water





# Conclusions

- Depending on temperature history and impurities glycerol can exhibit two different dynamic patterns:  
**with and without crystallization**
- The dynamical (**relaxation time**) and structural (**Kirkwood correlation factor**) properties of supercooled liquid glycerol are different for these two patterns
- The **pure dehydrated glycerol** exhibits crystallization at **263 K**  
Near this temperature the glycerol samples, which do not undergoes crystallization, exhibit some non-monotonic behavior of heat capacity
- The **dynamical crossover** temperature of glycerol could, similar to the water, lay above the temperature of crystallization while heating