The State Diagram of Foods: Physical Chemistry and Practical Implications

NTNU

Sustainable Energy in Food Production

MSTU

Norwegian University of Science and Technology

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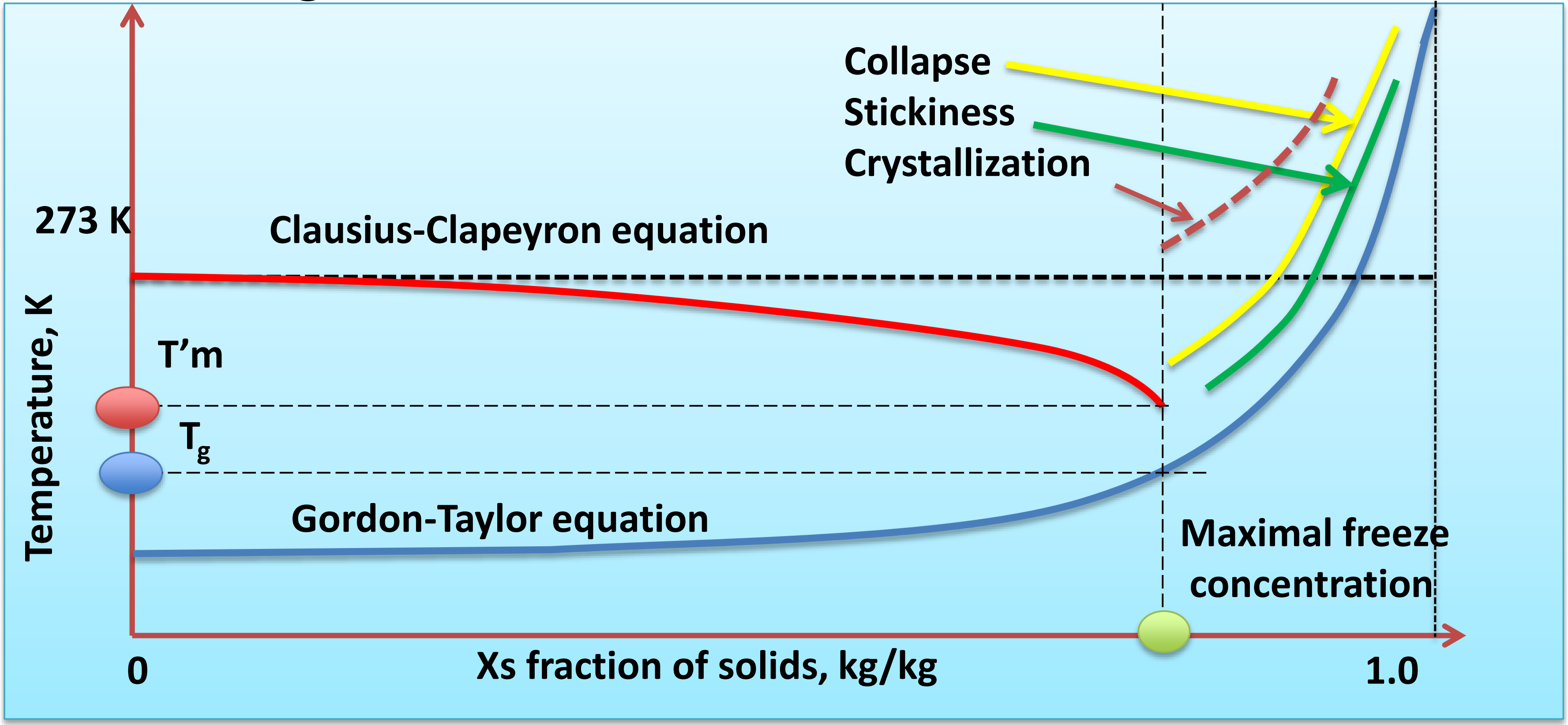
State diagram



State diagram

Clausius-Clapeyron equation

$$\delta = -\frac{\beta}{M_w}\ln\left(\frac{1 - x_s - Bx_s}{1 - x_s - Bx_s + Rx_s}\right)$$

Describes ice formation

Gordon-Taylor equation

$$t_{gi} = \frac{x_s t_{gi,s} + k x_w t_{gi,w}}{x_s + k x_w}$$

Describes Glass transition

2. Nature of the Glass transition

Glassy state is a second order thermal-phase transition. Which is common for carbohydrates, proteins, polymers and non-organic materials, even metal alloys.

The best examples of foods in a glassy state:

2. Nature of the Glass transition

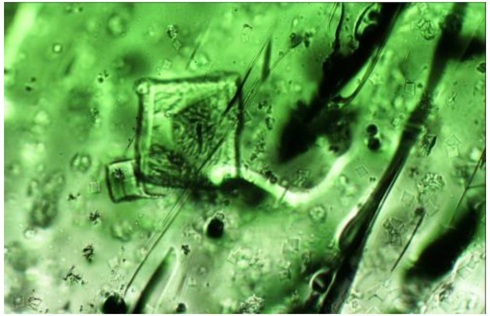
Glass is:

Solid and brittle like a crystal

Disordered structure

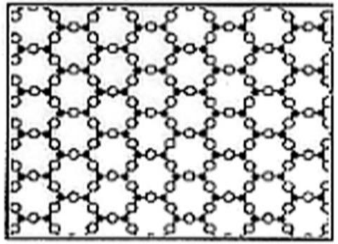
Looks like liquid but very viscous

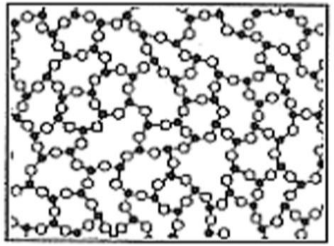
Most of materials shows both crystallization and glass transition



Crystal

Glass



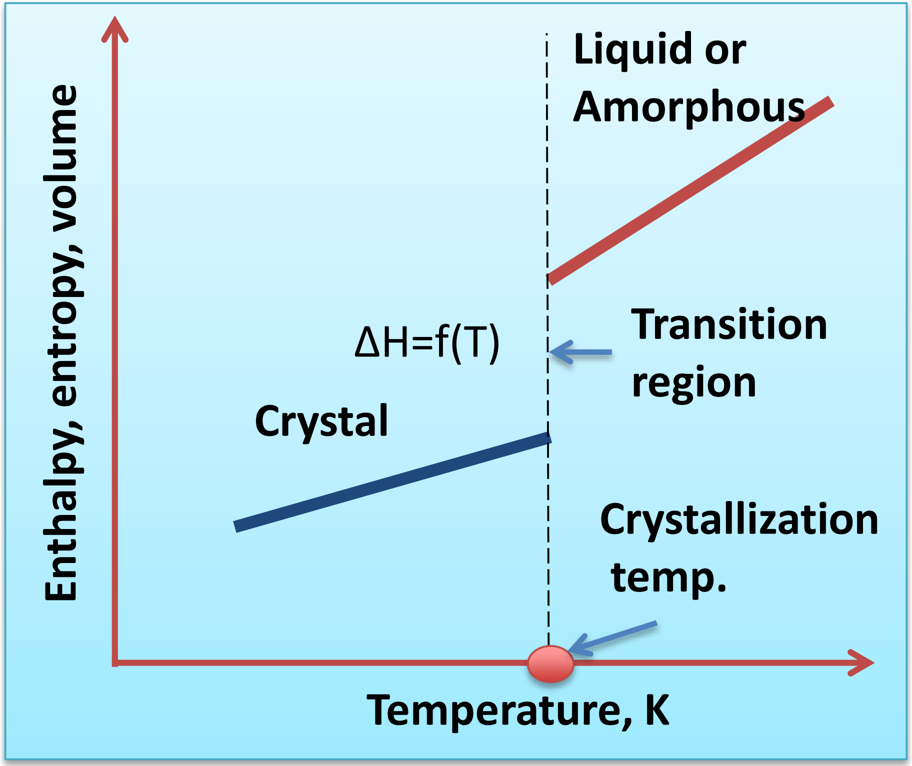


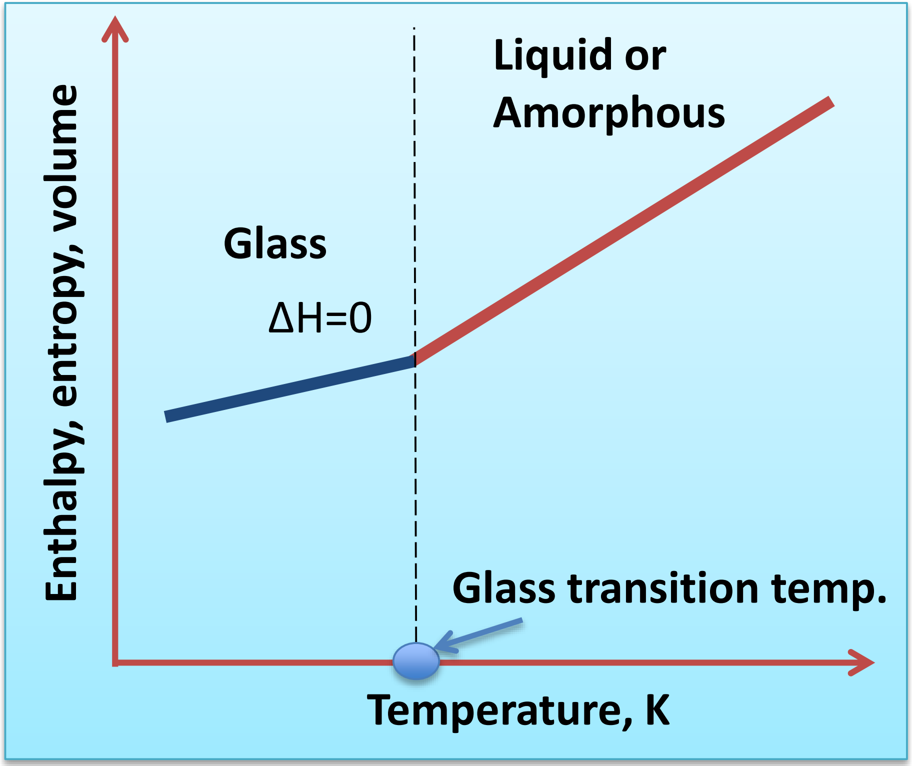
First order transition

Second order transition

2.1 The difference between first and second order transitions

Tcr>Tg

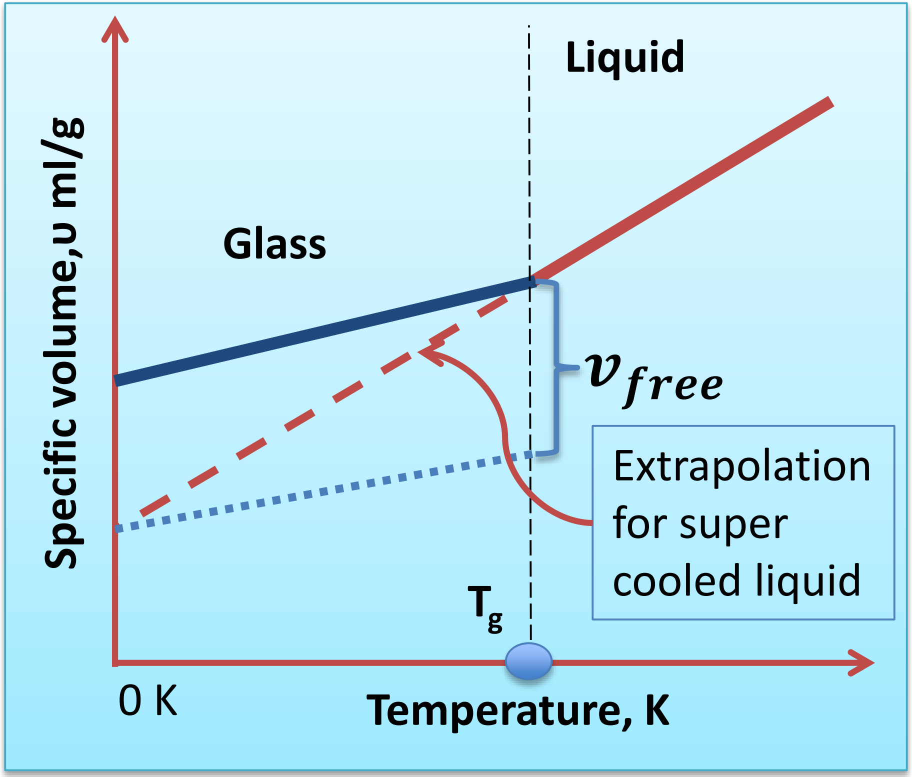




2.2. Main theories explaining the glass transition

- ❑ Free volume theory
- ❑ Kinetic theory
- ❑ Thermodynamic theory

2.2.1 Free volume theory



$$v_{total} = v_{molec.} + v_{free}$$

Free volume is decreasing with the temperature until it reaches the critical value

Below T_g the free volume is constant and independent from molecular weight

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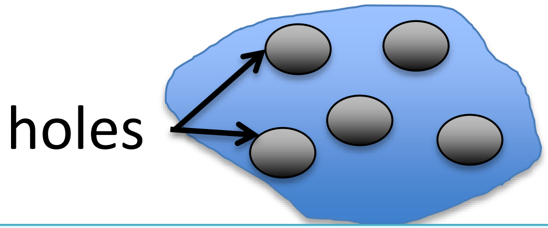
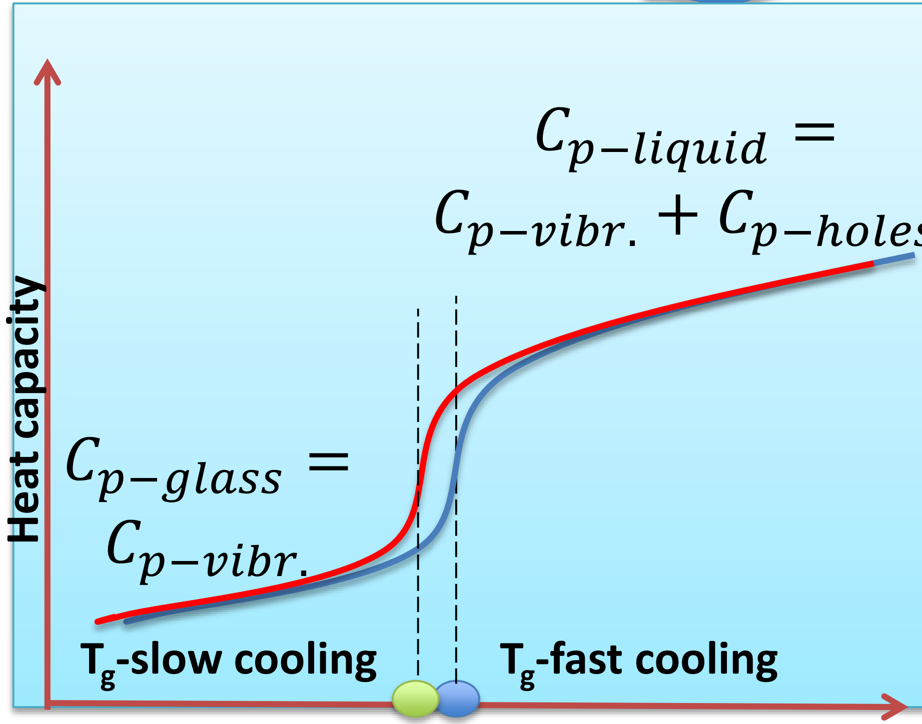
2.2.2 Kinetic theory



Matter includes holes, which permits long-amplitude molecular motion

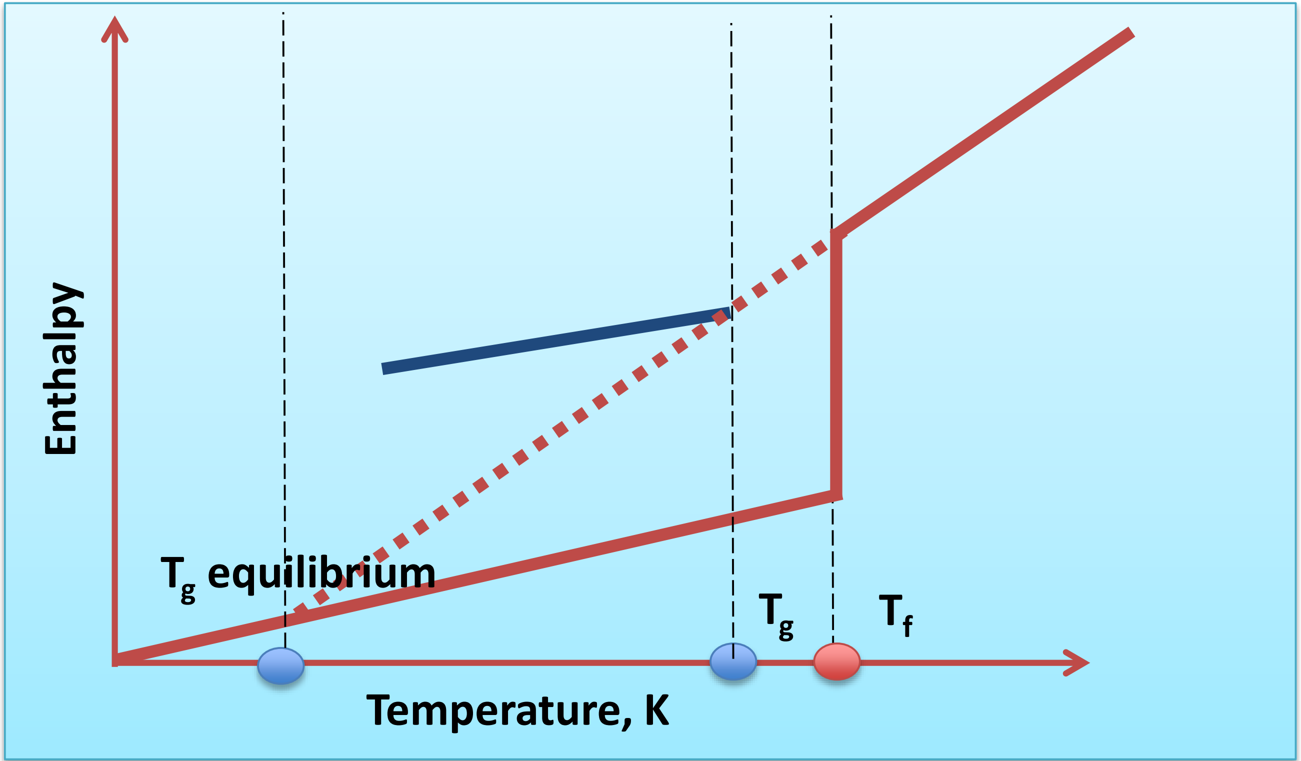
Equilibrium number of holes is a function of temperature

Creating, motion and destruction of holes takes time thus each cooling rate corresponds to freezing a different amount of holes. Hysteresis event as a result.



2.2.3 Thermodynamic theory

Infinitely long experiment leads to true equilibrium:



Enthalpy of glass transition will be in the range of enthalpy of crystal

2.3.1. Characteristics of the glassy state: viscosity

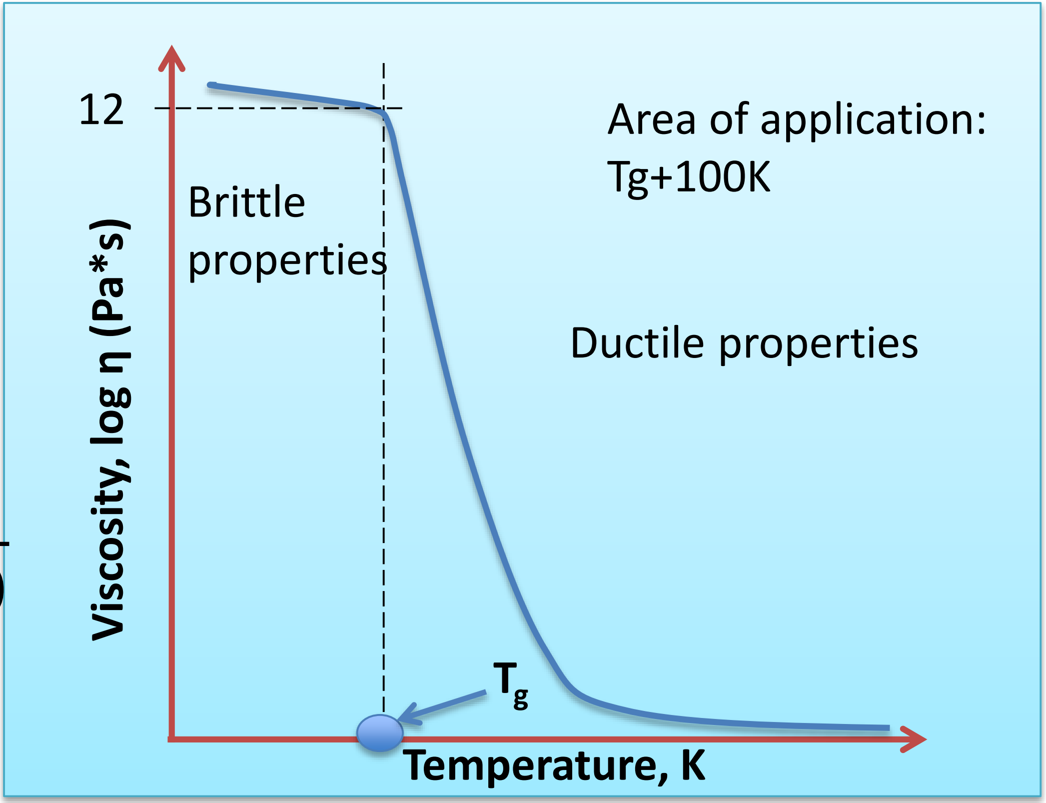
Vogel-Tamman-Fulcher (VTF) model

$$\eta_T = \eta_0 e^{\frac{BT_0}{(T-T_0)}}$$

Williams-Landel-Ferry (WLF) model

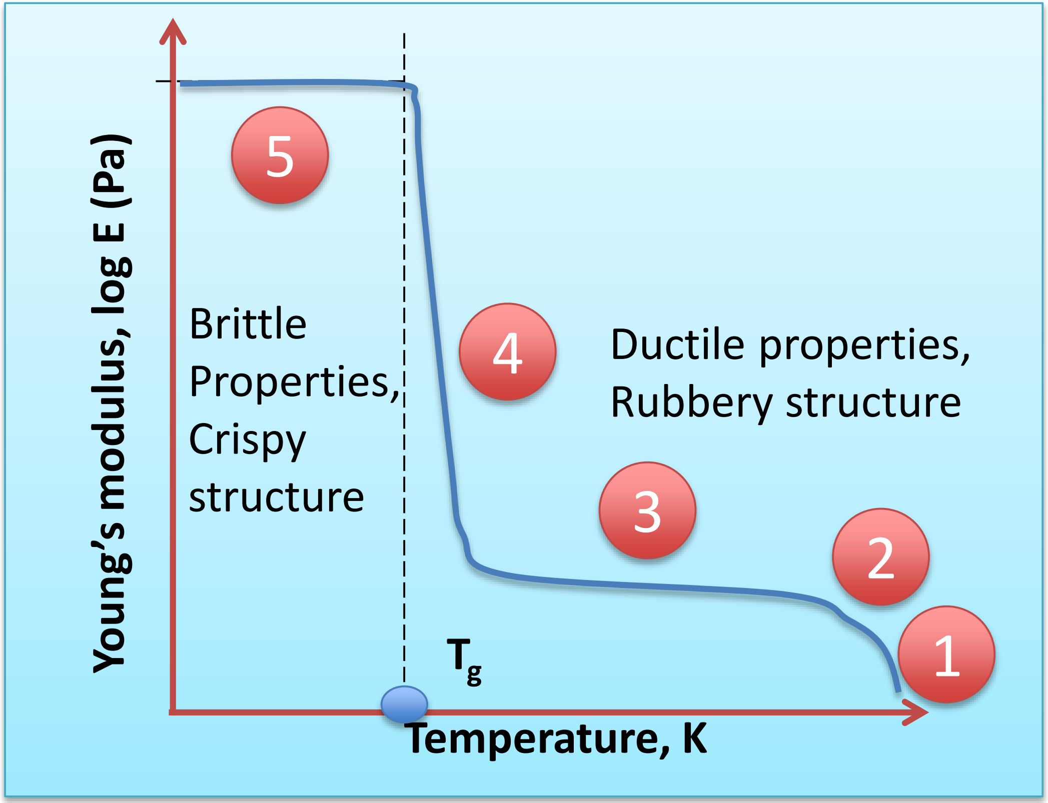
$$\log\left({}^{\eta_T}/_{\eta_{Tg}}\right) = \frac{C_1(T-T_g)}{C_2+(T-T_g)}$$

B, C1 and C2 – empirical constants



2.3.2 Characteristics of the glassy state: Rheological properties

1. Liquid flow
2. Rubbery flow
3. Rubbery plateau
4. Glass transition region
5. Glassy state

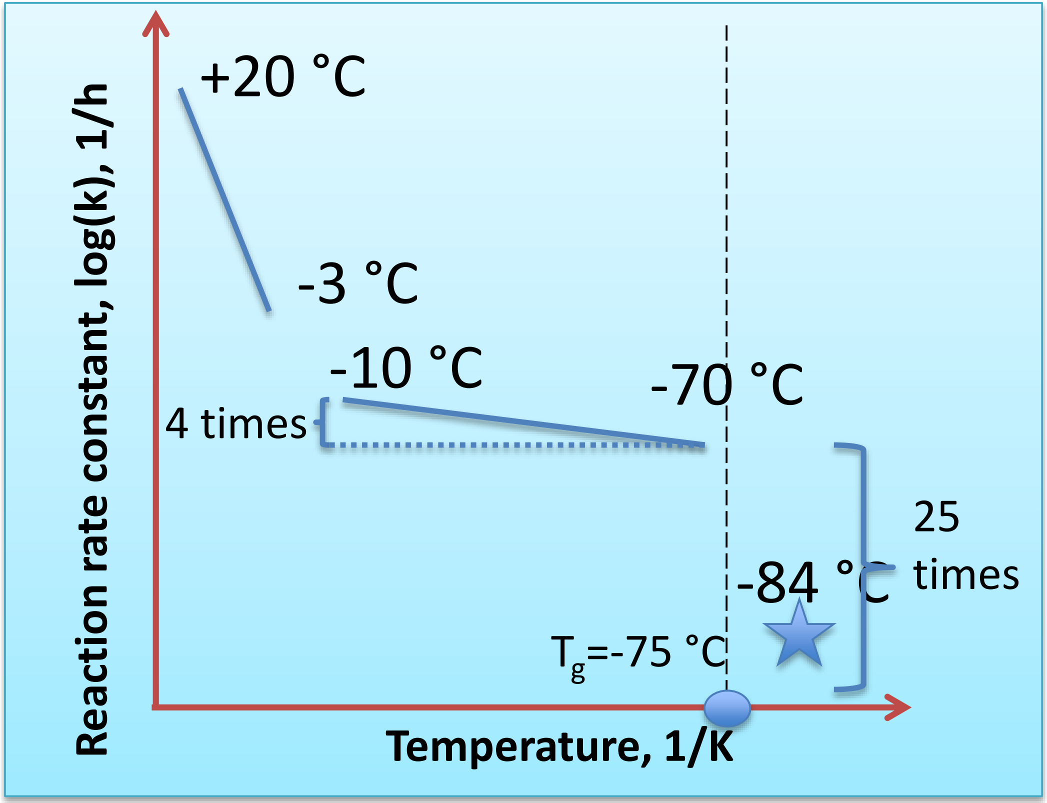


2.3.3 Characteristics of the glassy state: Reaction rate in foods

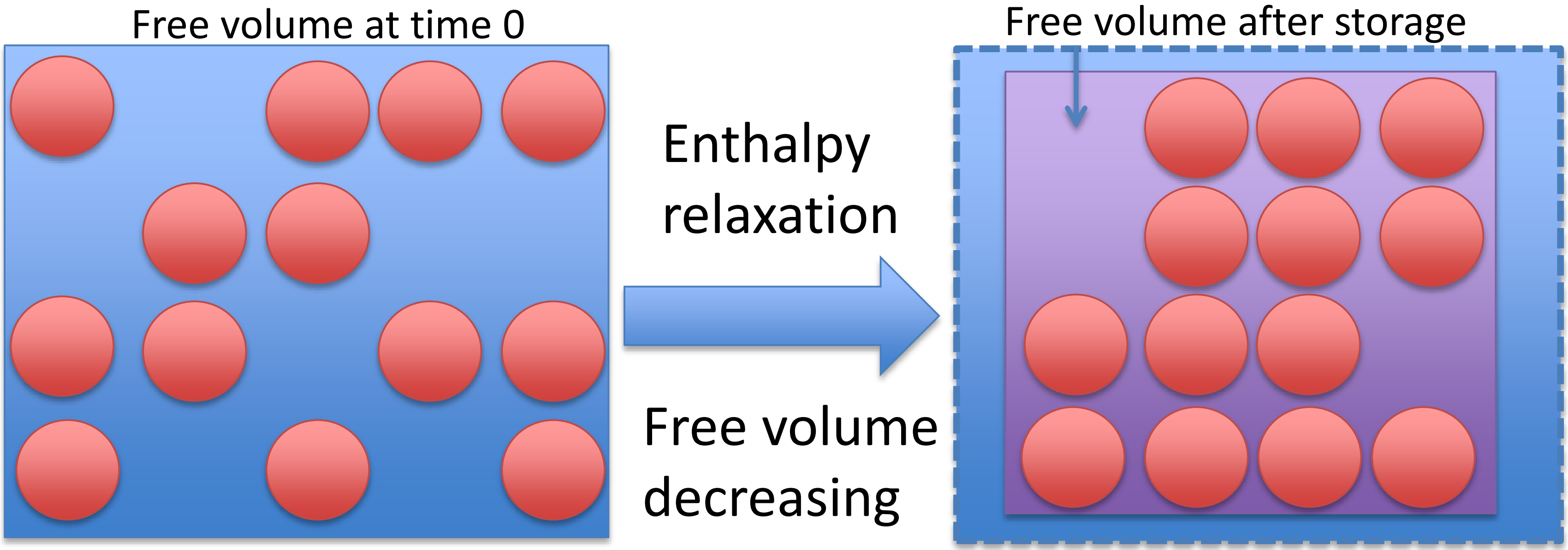
Example of reaction rate constant
vs temperature for k-value of tuna meat

$$k = k_0 e^{\frac{-Ea}{RT}}$$

!!! In low moisture food, which are stored at room temperature, other factors influence on the reaction rates!!!

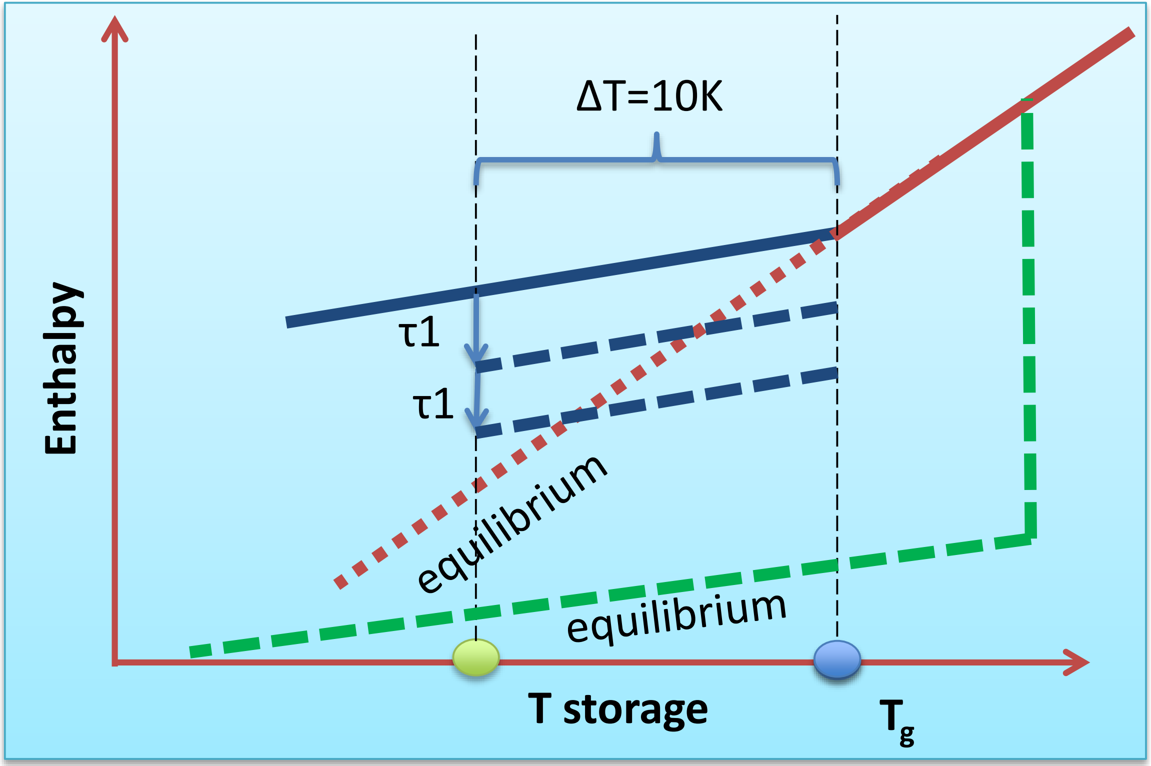


2.3.4 Characteristics of the glassy state: Aging. The relaxation during storage



The process depends on the structure of material, storage temperature and time

2.3.4 Characteristics of the glassy state: Aging. The relaxation during storage



Aging leads to the alteration of material's structure

For some materials physical stability appears at 50 K below T_g

Sugars, cereal products

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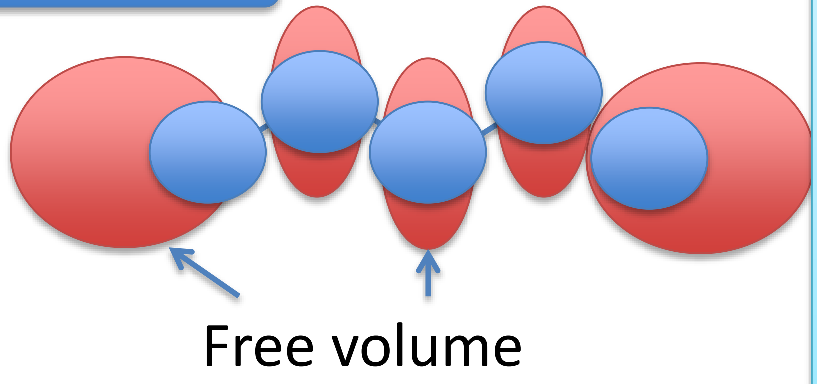
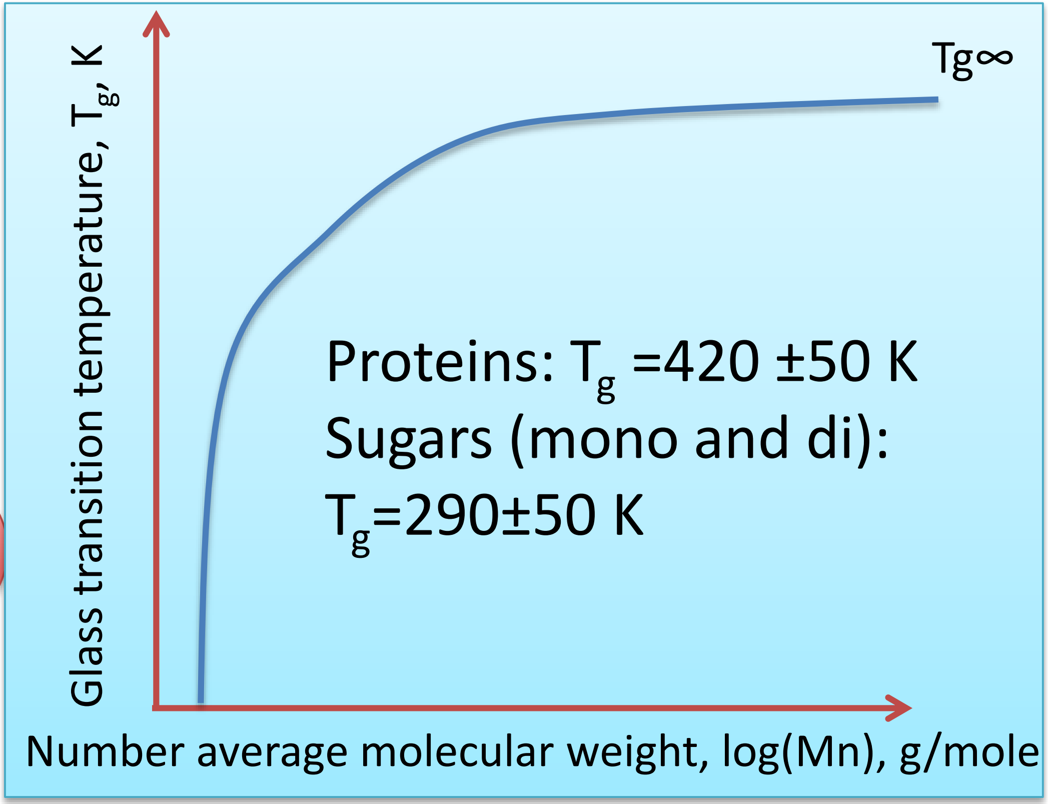
3.1. Factors influencing the glass transition in foods: molecular weight:1

Flory-Fox equation

$$T_g = T_{g\infty} - \frac{K}{M_n}$$

Molecule





3.1. Factors influencing the glass transition in foods: molecular weight:2

Material	Glass transition, °C
Ethanol	-183..-177
Water	-135..-142
Glucose	20..30
Sucrose	67
Starch	151..215

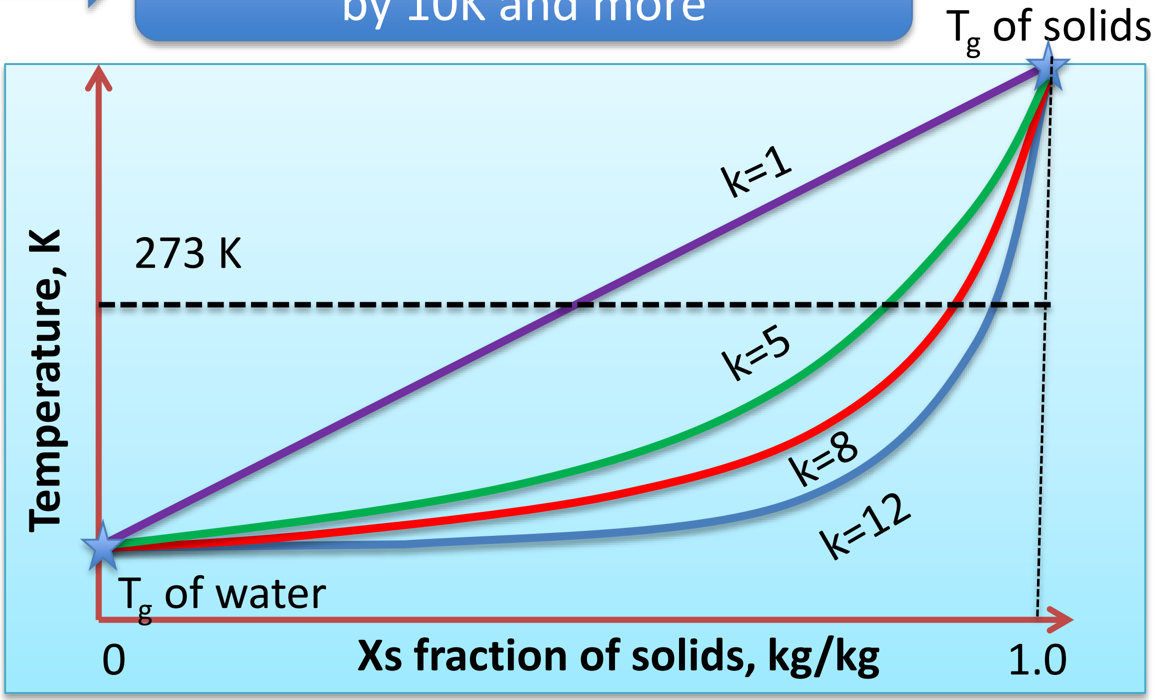
This is pure material, the Tg in the real food will be influenced by the water content

3.2. Factors influencing the glass transition in foods: Plasticizers

Water → 1 % of water will decrease the T_g by 10K and more

Gordon-Taylor equation

$$T_g = \frac{x_s T_{g,s} + k x_w T_{g,w}}{x_s + k x_w}$$



3.3. Factors influencing the glass transition in foods: Rate of freezing

Most of the foods crystallizes before glass transition

Sugar crystal formation

Ice formation

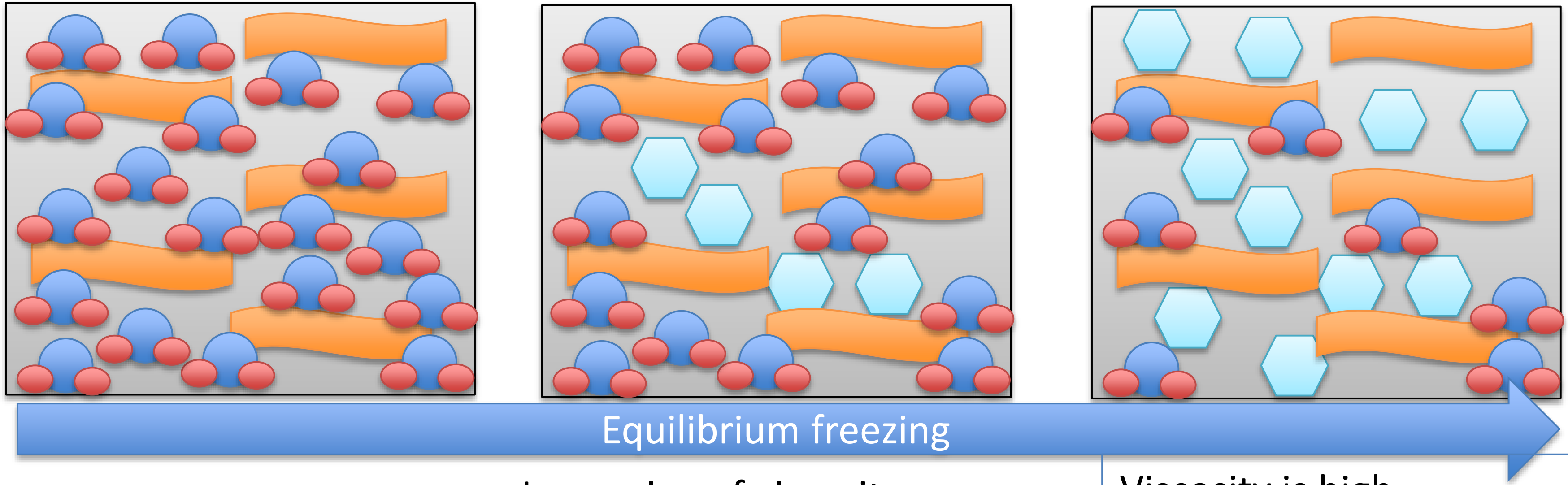
Fast cooling can help to avoid that

T_g at higher temperatures, (kinetic theory)

T_g at lower temperatures, (Gordon-Taylor dependence)

3.4. Factors influencing the glass transition in foods: Maximal freeze concentration

Maximal freeze concentration



Low viscosity

Increasing of viscosity
during water removing process
(freezing or drying)

Viscosity is high,
$10^7..10^8$ Pa*s
Ice formation is stopped, T’m

Maximal freeze concentration depends on the food composition, between 10 and 40 % w.b.

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3. Glass transition in foods

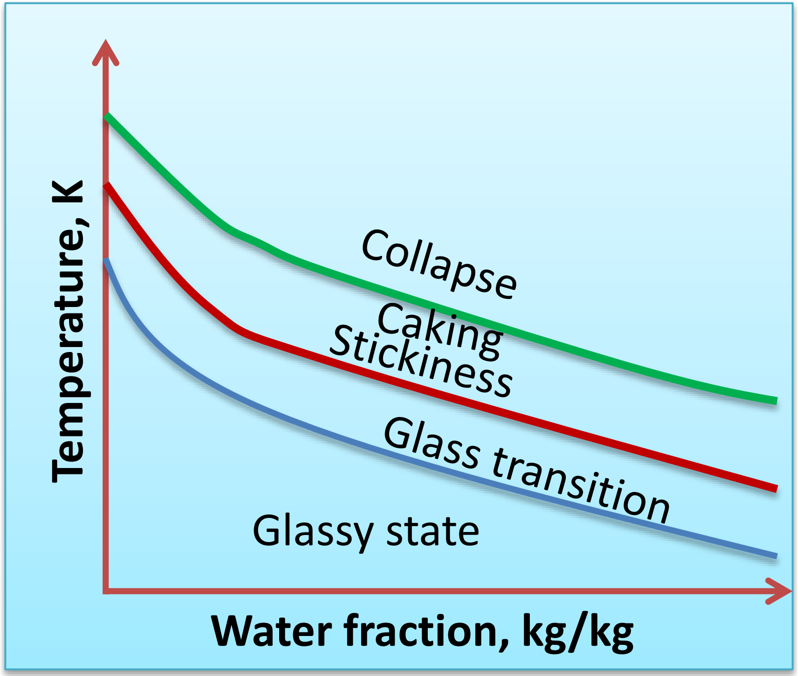
Can be obtained by:

Rapid cooling (candies, starch products etc.)

Evaporation of water or other plasticizer until reaching the maximal freeze concentration

Freezing of water until reaching the maximal freeze concentration

4.1 Glass transition in foods: dried foods



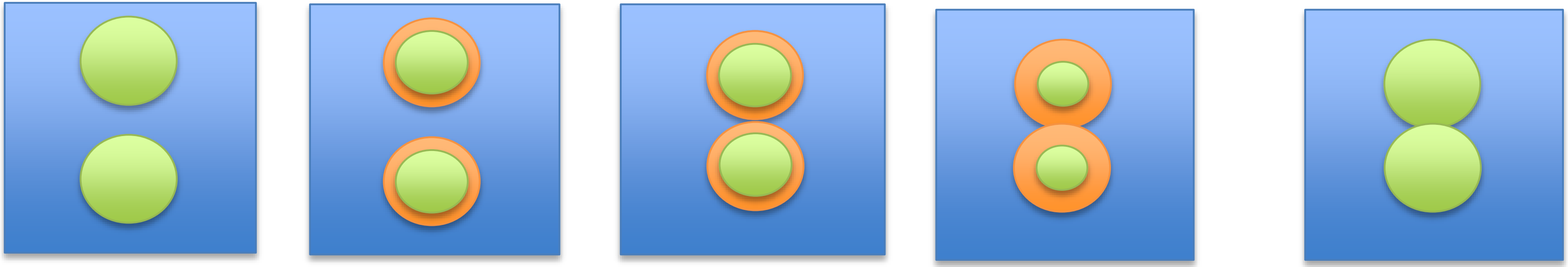
All processes are above T_g

Stickiness – due to plasticizing the particles surface, the viscosity is low enough for adhesion

Caking – agglomeration of sticky particles

Collapse – the viscosity of the system so low, that can not support the structure of the food.

4.2 Glass transition in foods: stickiness and caking (low moisture foods)



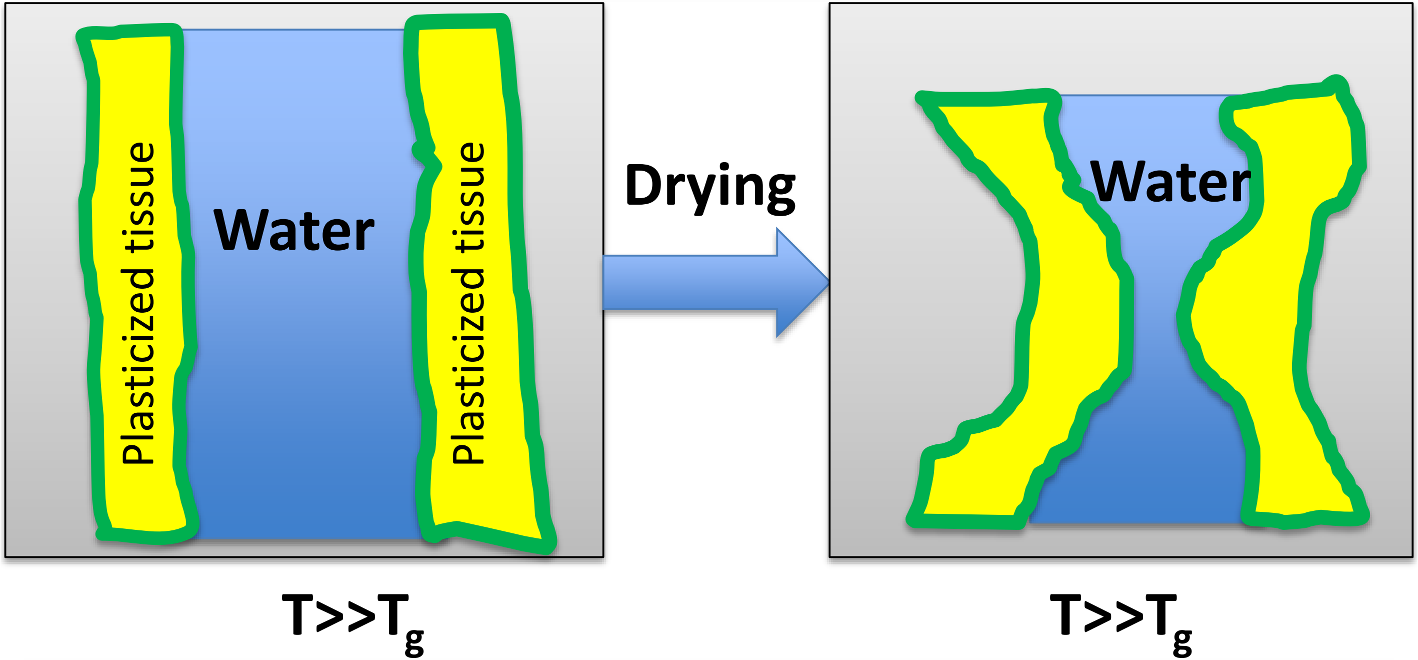
$T<T_g$	$T>T_g$	$T>T_g$	$T>T_g$	$T<T_g$
Free flowing particles	Plasticized surface	Attraction	Agglomeration	Cooling and/or dewatering

Caused by: increasing or the temperature and/or moisture content

Can be used as a benefit!!!

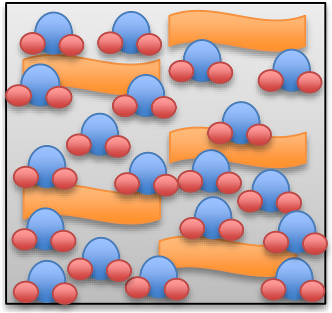
4.3 Glass transition in foods: collapse

The same mechanism as for agglomeration

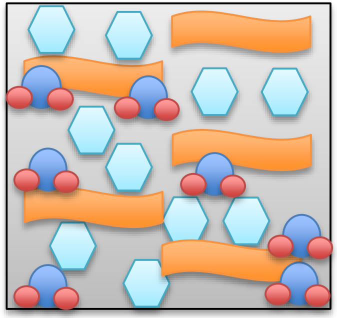


Viscous flow of the plasticizes tissue. Process is time and temperature dependent.

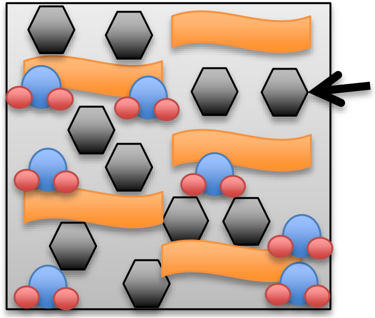
4.4 Glass transition in foods: freeze drying



Fresh product



Frozen product below T’m



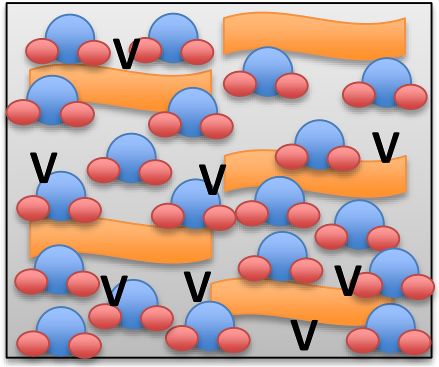
Holes after ice crystal evaporation

Dried product, below T_g

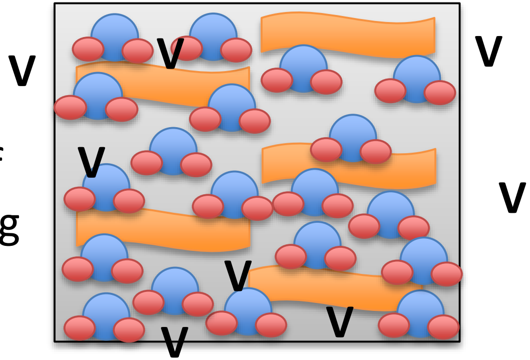
Exposition of the material at temperatures higher than higher T’m leads to plasticizing of the material. This cause the defect of structure due to collapse.

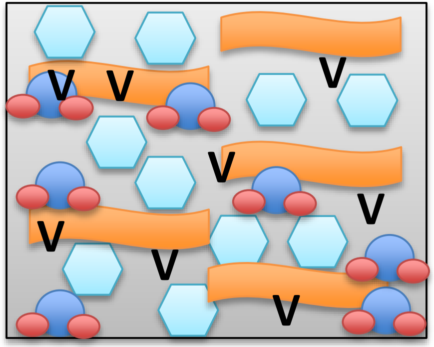
4.5 Glass transition in foods: volatiles entrapping

Glassy matrix is selectively permeable for water, but not permeable for volatiles=> conserved flavor

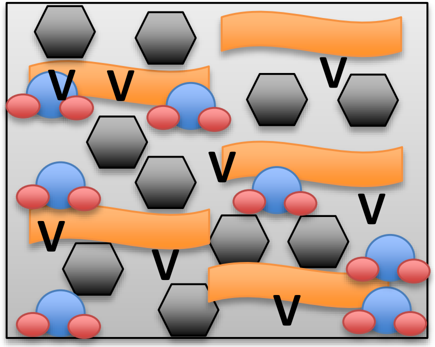


Diffusion and evaporation of the volatiles during air-drying

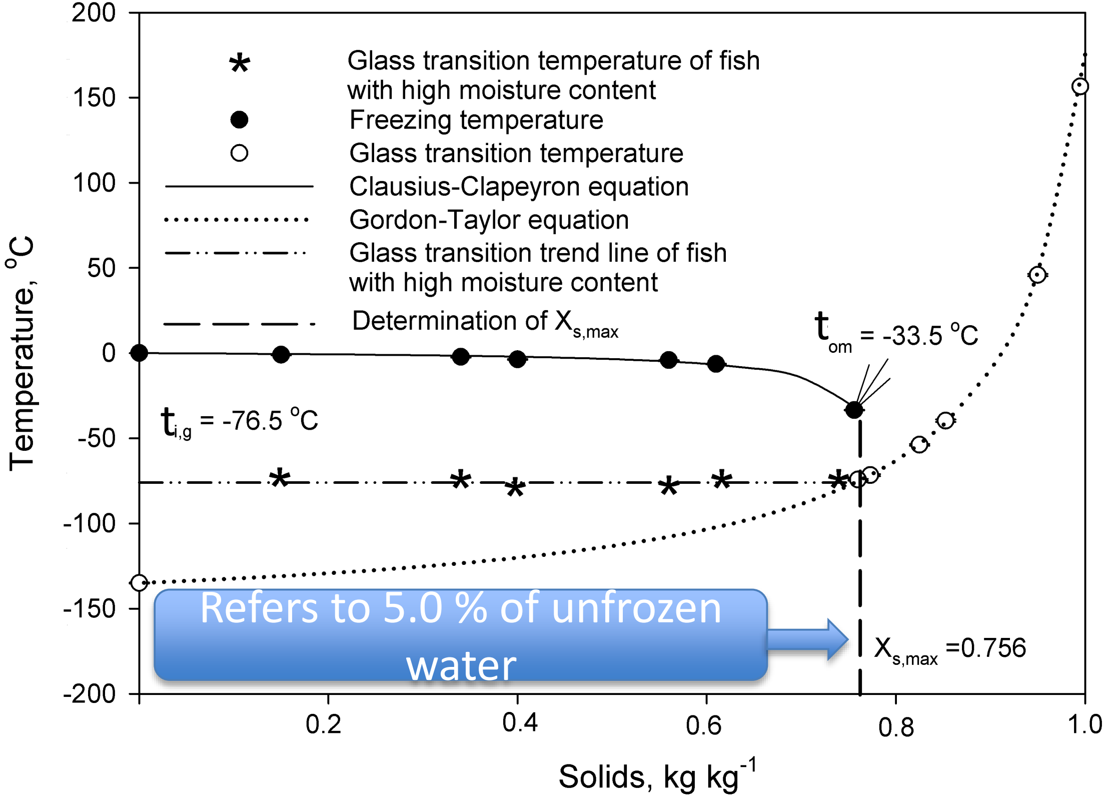




Volatiles are trapped by the freeze-consentrated matrix



Cod muscles



State diagram for cod muscles

Clausius-Clapeyron equation

$$\delta = -\frac{\beta}{M_w}\ln\left(\frac{1 - x_s - Bx_s}{1 - x_s - Bx_s + Rx_s}\right)$$

Gordon-Taylor equation

$$t_{gi} = \frac{x_s t_{gi,s} + k x_w t_{gi,w}}{x_s + k x_w}$$

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4. Conclusions

? Any ideas ?

How would you apply state diagram in freeze drying, drying freezing?