Strategies for Probing Water and Solids Mobility in Food Materials

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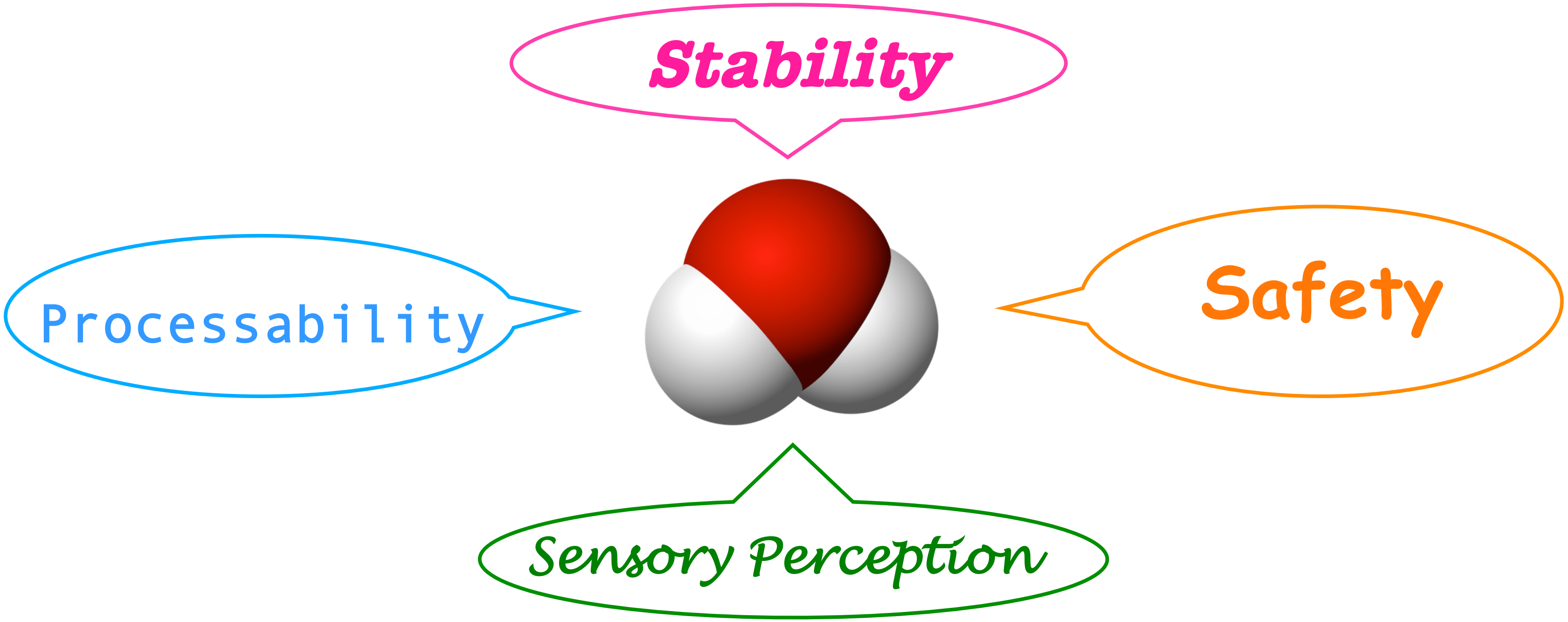
Water is an important component of all foods

Two key aspects:

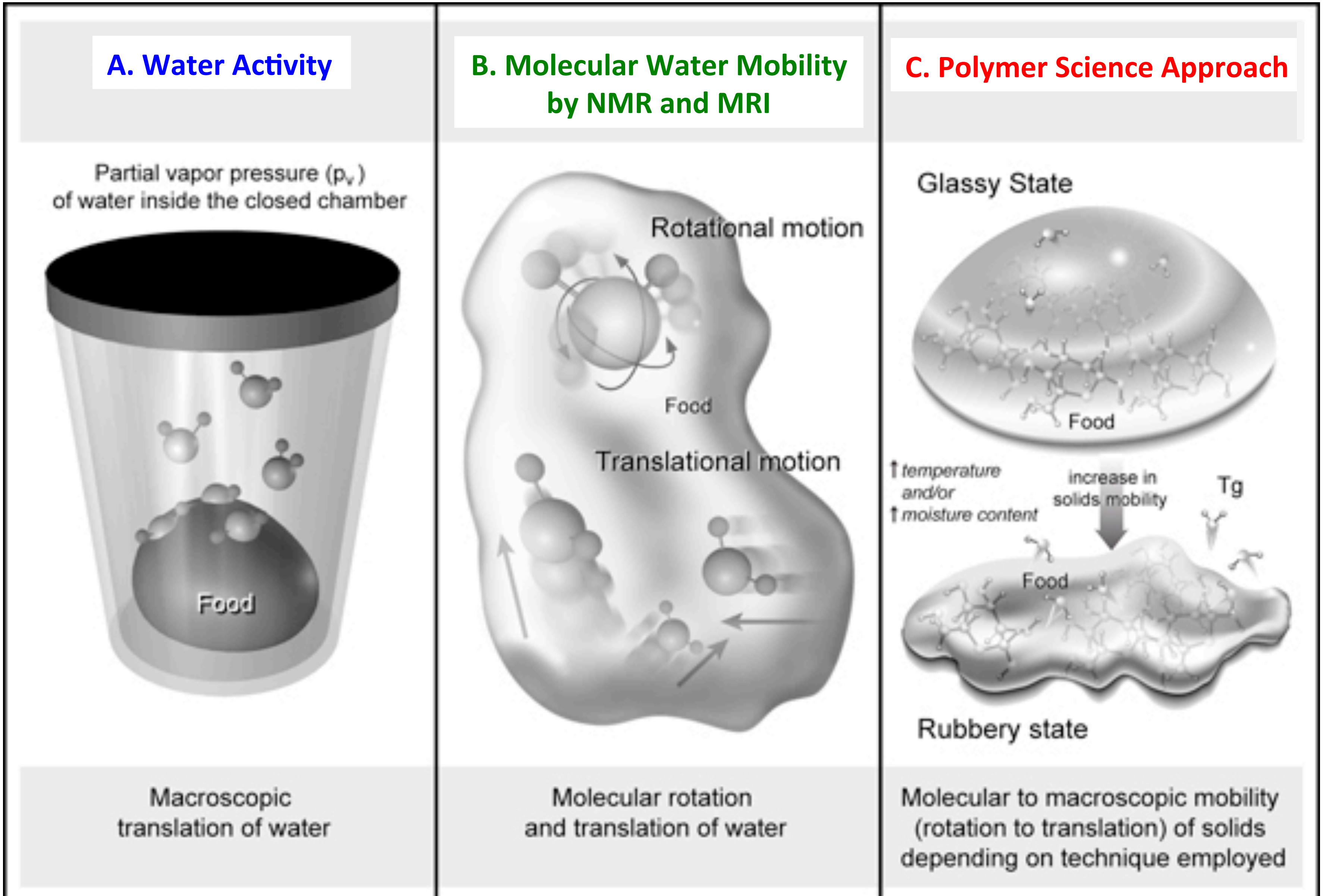
Q. How much water is present?

Q. What impact does this water have on the processability, stability, safety, and sensory perception of the food system?



Introduction

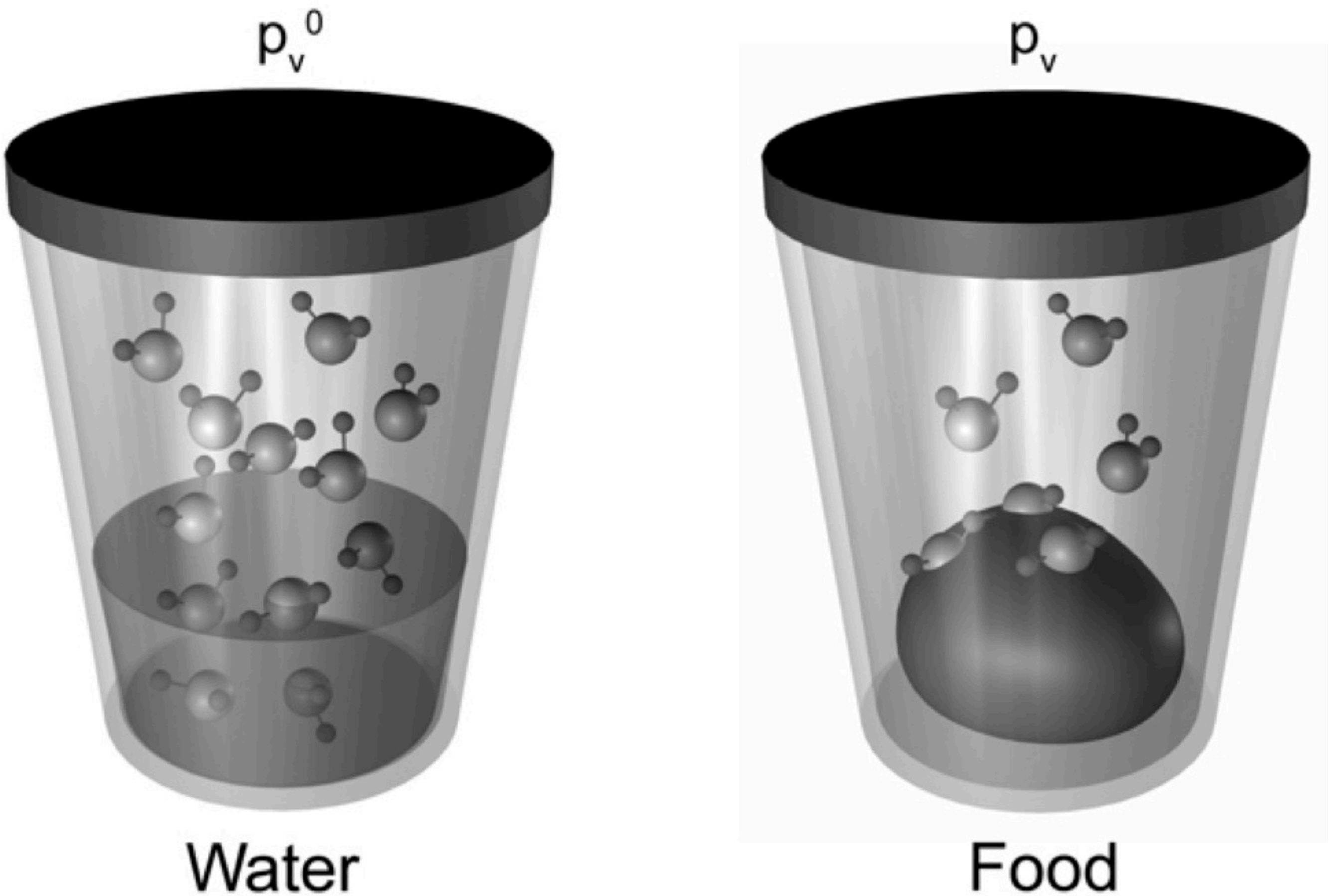
Three Main Strategies for Probing Water and Solids Mobility



Fundamental Principles

The concept of substance "activity" was derived by Gilbert Lewis in 1907 from the laws of equilibrium thermodynamics.

$$a_{wFood} = a_{wVapor} = \frac{p_v}{p_v^0} = \frac{\%ERH}{100}$$



Assumptions:

1. At equilibrium
2. Constant T & P

Macroscopic translational mobility of water (minutes to hours)

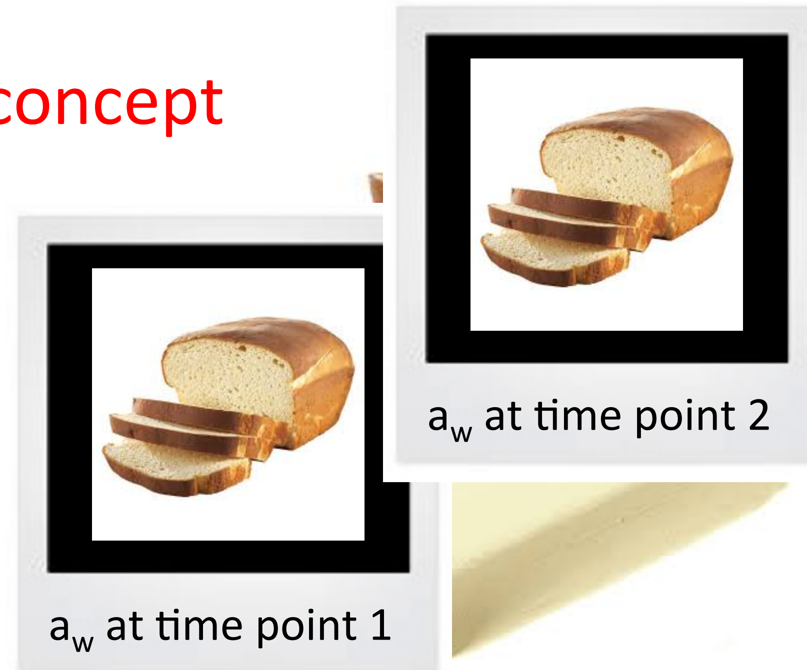
Fundamental Principles

Assumptions underlying the a_w concept

1. Thermodynamic equilibrium

   Food system - depends on system

   a_w measurement - YES!



2. Conditions of constant temperature and pressure

   Most food ingredients and systems: as T $\uparrow$ a_w $\uparrow$

   Except high concentrations of sugars and salts: as T $\uparrow$ a_w $\downarrow$

Subfreezing Temperatures

a_w above freezing:

$$a_w = \frac{p_v}{p_v^o}$$

Composition and Temperature

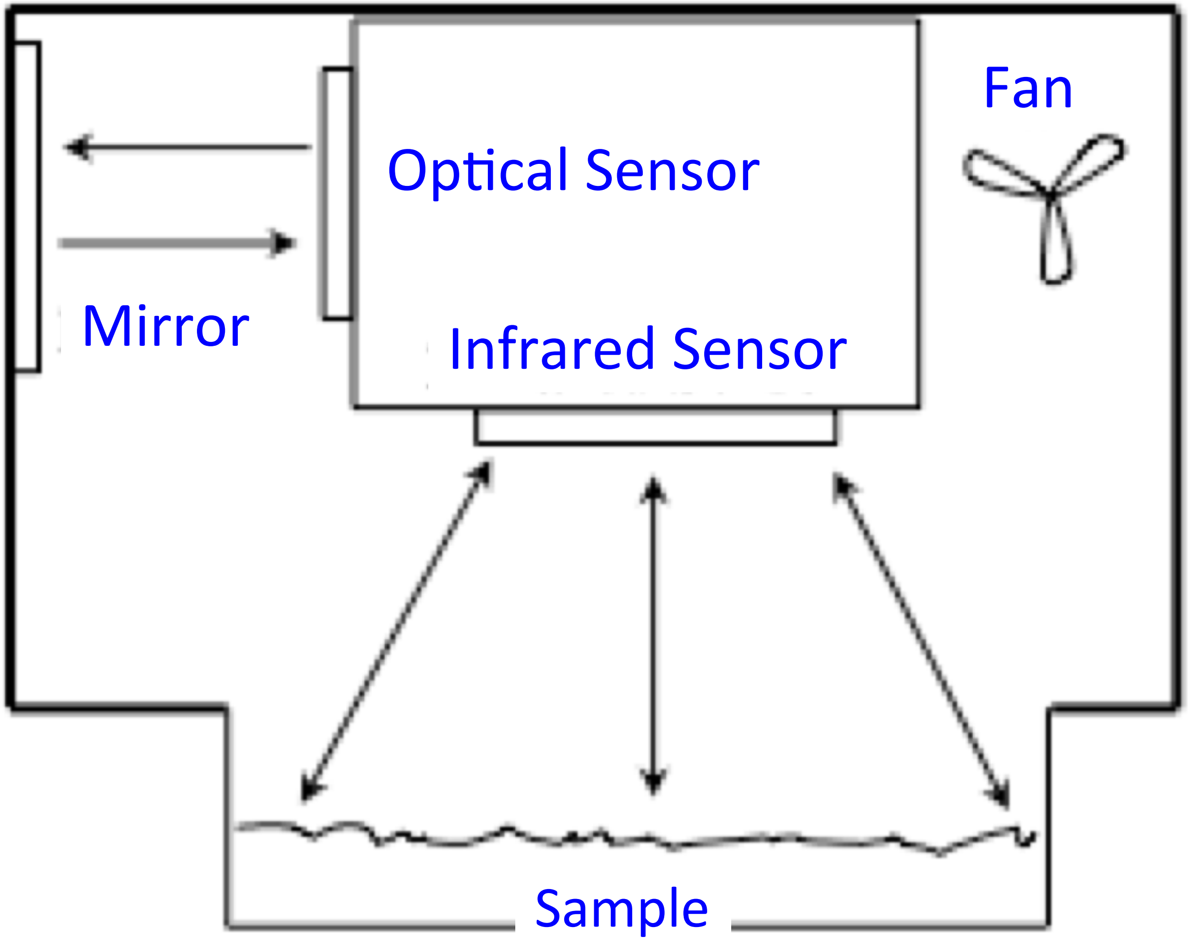
a_w below freezing:

$$a_w = \frac{p_{ice}}{p_{SCW}^o}$$

Temperature

Measurement Methods: Direct

Chilled Mirror Dew Point Hygrometer



Chilled Mirror Dew Point Hygrometer

Advantages

1. Primary method of measuring vapor pressure
   Not calibrated, but rather verified with salt solutions
2. Highest accuracy ±0.003a_w
3. Rapid measurement < 5min
   The time depends on the nature of the material. Glassy samples greatly increase the measurement time.
4. Measures entire a_w range (0.03 to 1.0)
5. Temperature controlled [e.g., 15 to 50°C (± 0.2°C)]
6. High reliability – natural variability in biological materials is challenging

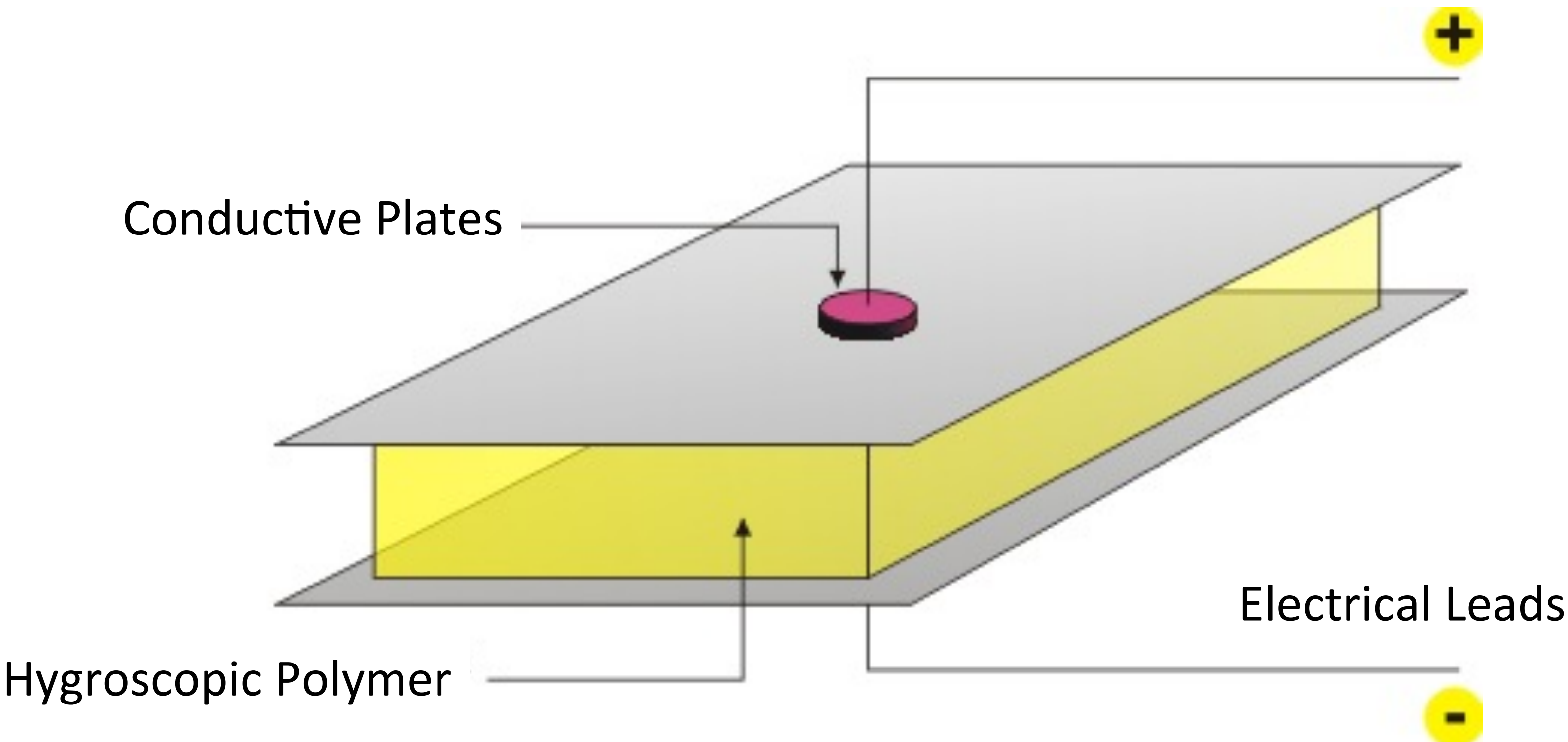
Disadvantages

1. Need to regularly clean mirror
2. Readings may be affected by alcohol and propylene glycol – research to eliminate this on going

It is important to develop a consistent, robust protocol for measuring a_w of your samples that minimizes uncertainty.

Measurement Methods: Indirect

Electronic Hygrometers - Two types: Resistance and Capacitance – both material properties change as a function of relative humidity



Electronic Hygrometer

Advantages

1. Good accuracy ($\pm 0.015 a_w$)
2. Relatively insensitive to volatiles
3. Measures entire a_w range
4. Usually lower cost

Disadvantages

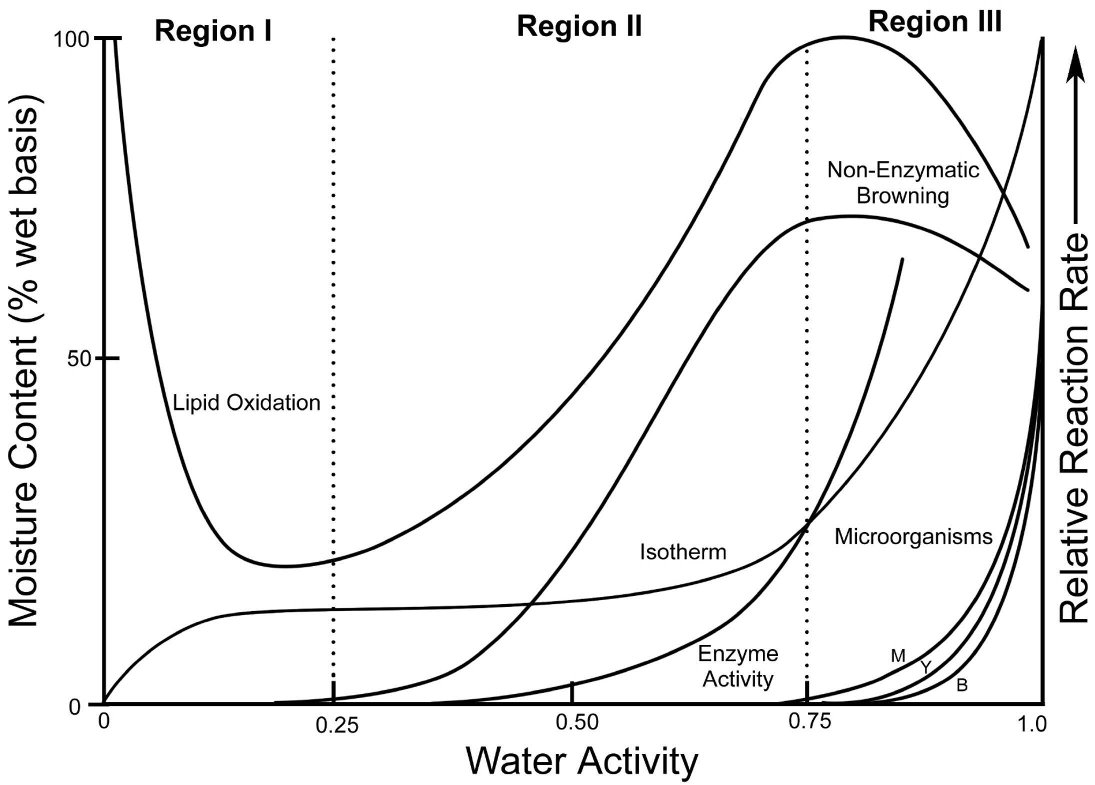
1. Needs calibration (indirect method)
2. Needs temperature compensation for sensor
3. Some sensor hysteresis overtime

It is important to develop a consistent, robust protocol for measuring a_w of your samples that minimizes uncertainty.

Strengths and Limitations

Strengths

- Quick and easy measurement with little or no sample preparation or pretreatment
- Requires low cost equipment ₵ and minimum operator training
- Established and successful record of use correlating a_w and isotherm behavior (mc versus a_w) to food stability issues, especially microbial growth and moisture migration in dual textured foods



Strengths and Limitations

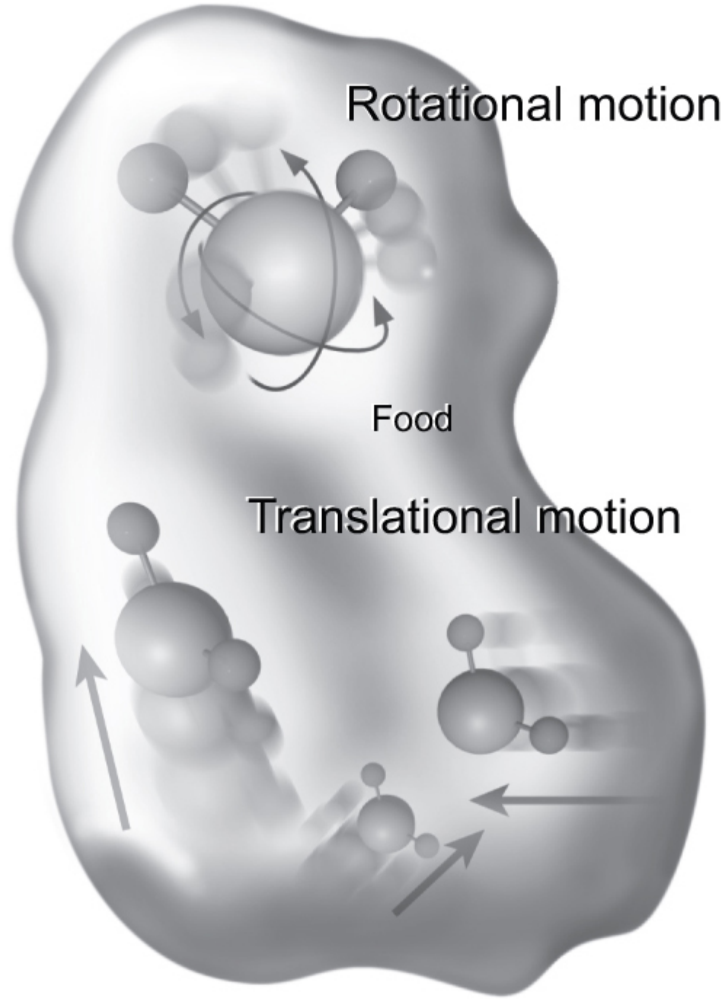
Limitations

- Some foods violate the assumption of thermodynamic equilibrium underlying the development of the a_w concept

- Not always an adequate predictor of food stability
- Not useful below freezing to predict product stability

Fundamental Principles

NMR and MRI provide nuclei, in the presence of a magnetic field, with a radiofrequency pulse of energy and measure the relaxation response of the nuclei over time. This response is then related to the molecular mobility of the nuclei probed.

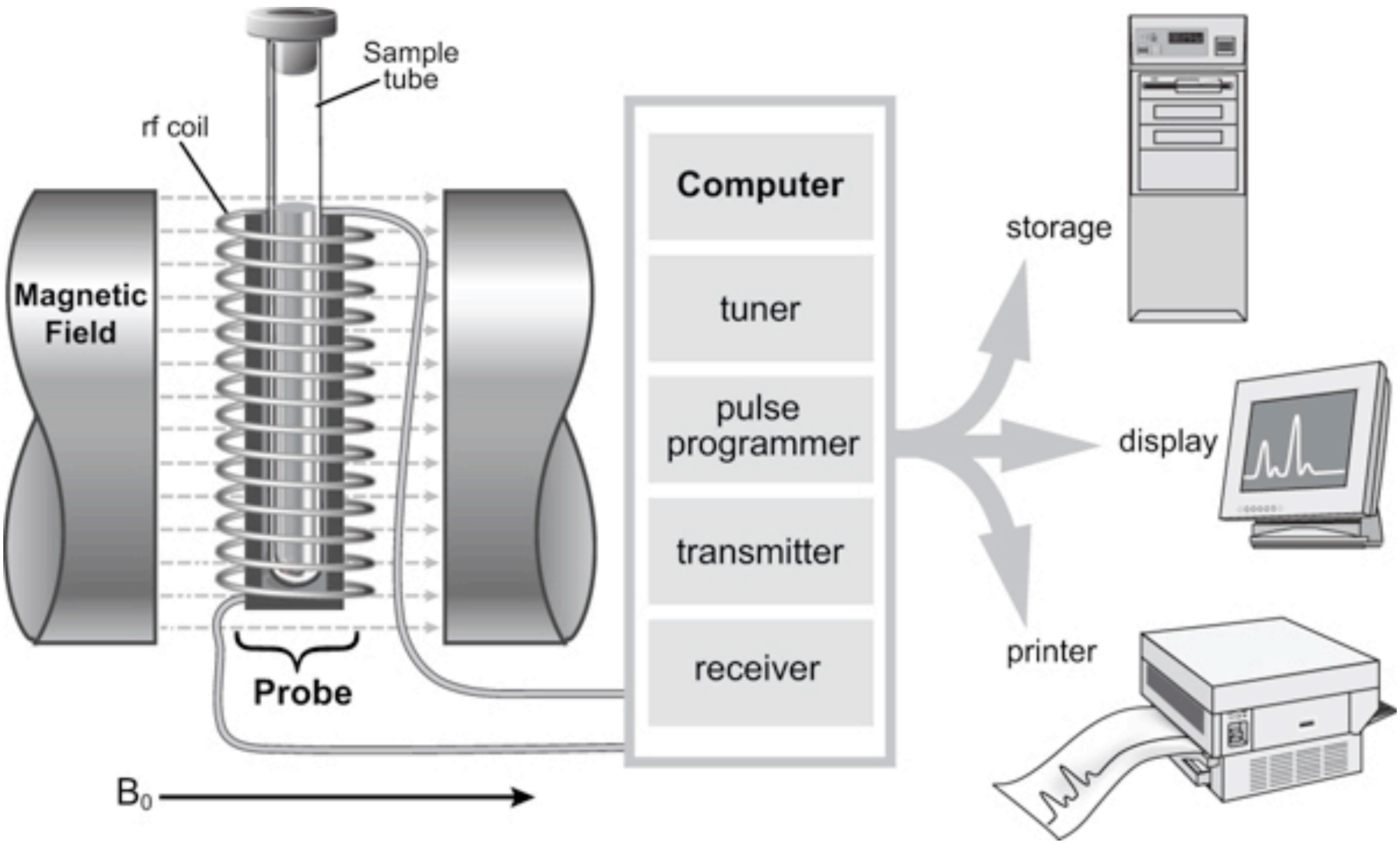


Water nuclei: ^{1}H, ^{2}H, or ^{17}O

Molecular rotation and translation of water (picoseconds to minutes)

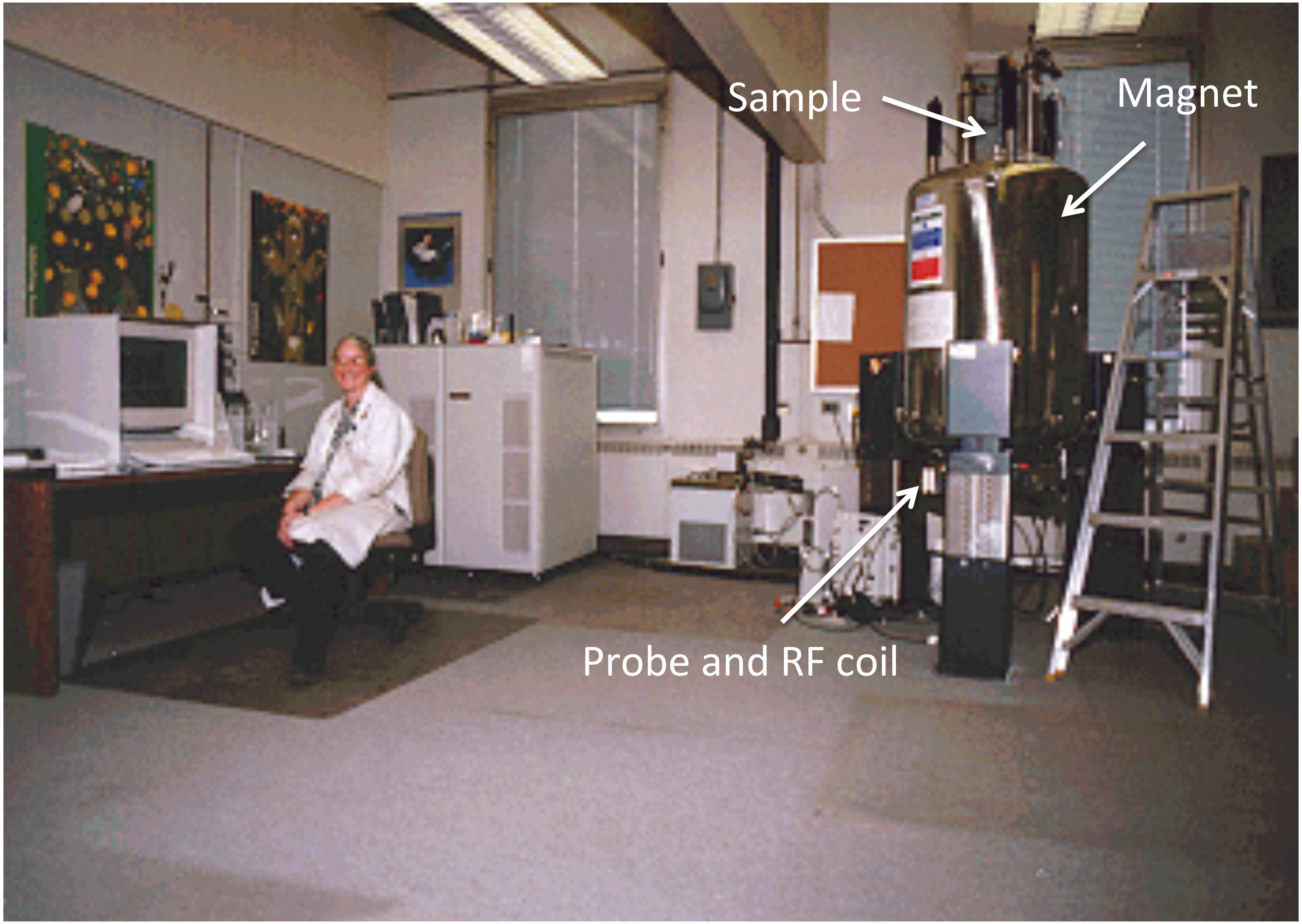
Measurement Methods

Basic Nuclear Magnetic Resonance spectroscopy components



Measurement Methods

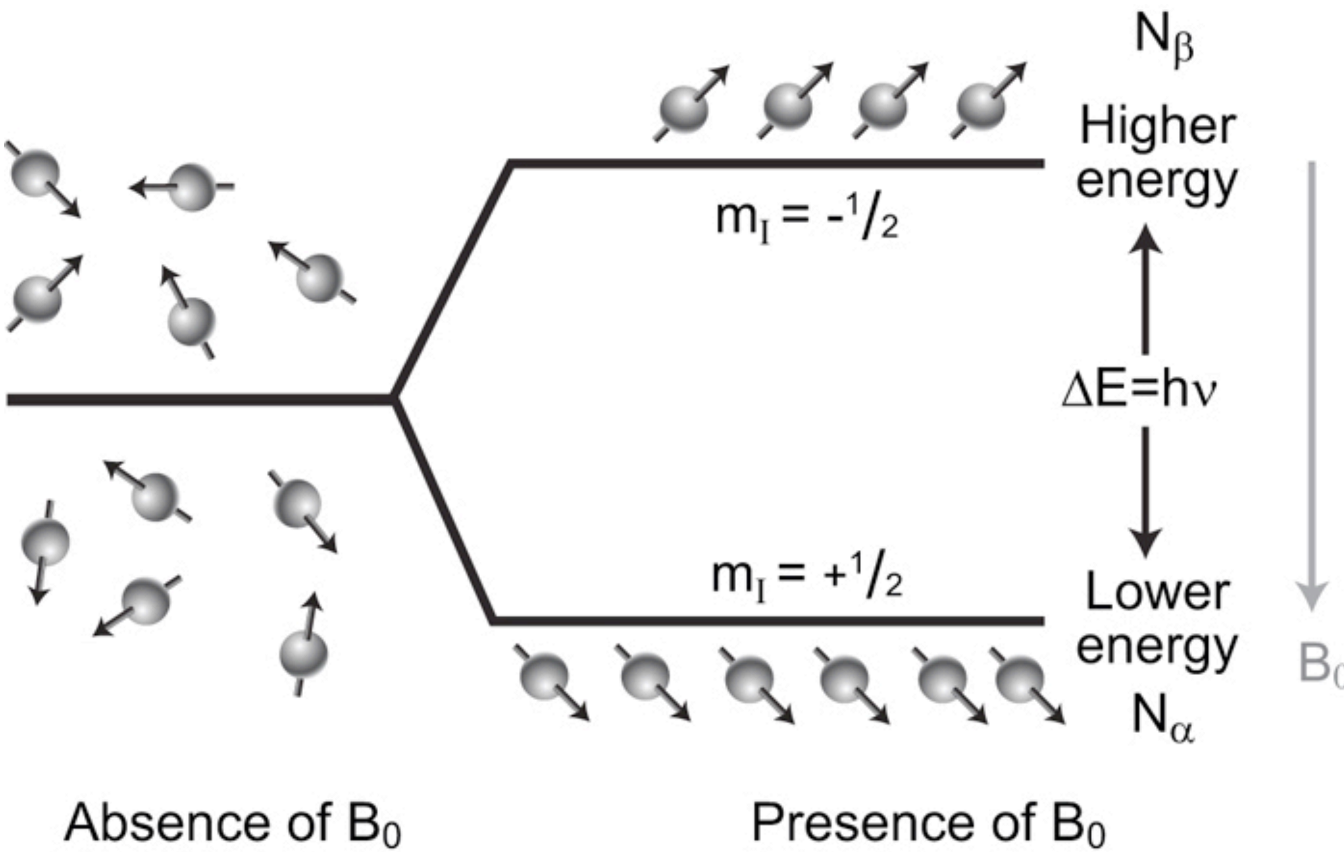
Basic Nuclear Magnetic Resonance spectroscopy components



Water Mobility by NMR and MRI

Measurement Methods

Schematic illustration of a basic one pulse ^{1}H NMR experiment



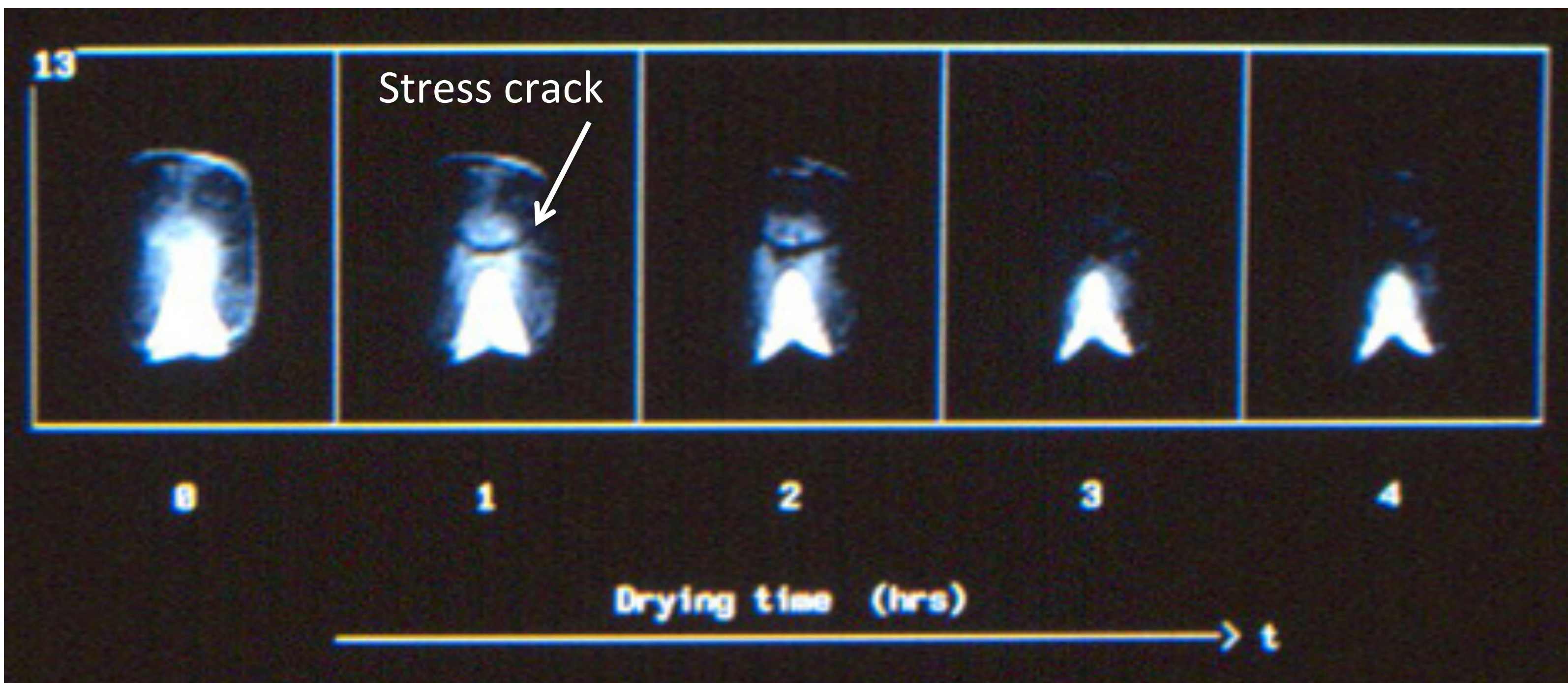
Once aligned in the magnetic field, the lower energy nuclei are given an RF pulse, which causes them to align against B_0. The relaxation time of these nuclei is then related to their mobility. Slow relaxation, more mobility; fast relaxation, less mobility. NMR is 1D, whereas MRI is 3-D.

Other options for measuring mobility include, Electron spin resonance (ESR) and Optical luminescence

Strengths and Limitations

Strengths

- Non-invasive, non-destructive method that probes the molecular mobility of water inside virtually any food sample with little or no preparation or pretreatment
- Characterizes water dynamics and distribution in food materials as affected by various events and processes

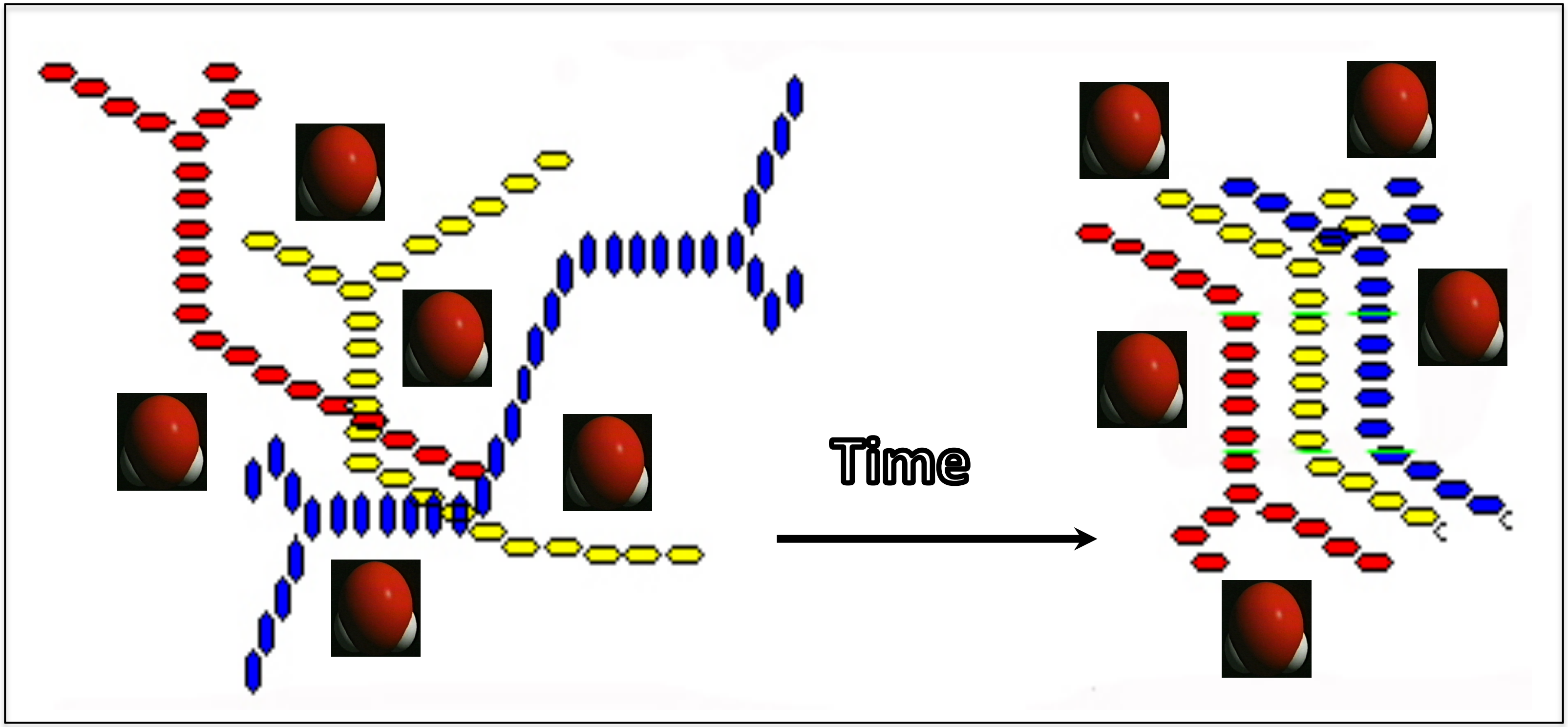


Strengths and Limitations

Strengths (con't)

- Can provide molecular level insight into the mechanism(s) underlying food stability and quality issues

Example: Quantify the mobility of the water and the amount and mobility of starch as it retrogrades over time



Strengths and Limitations

Limitations

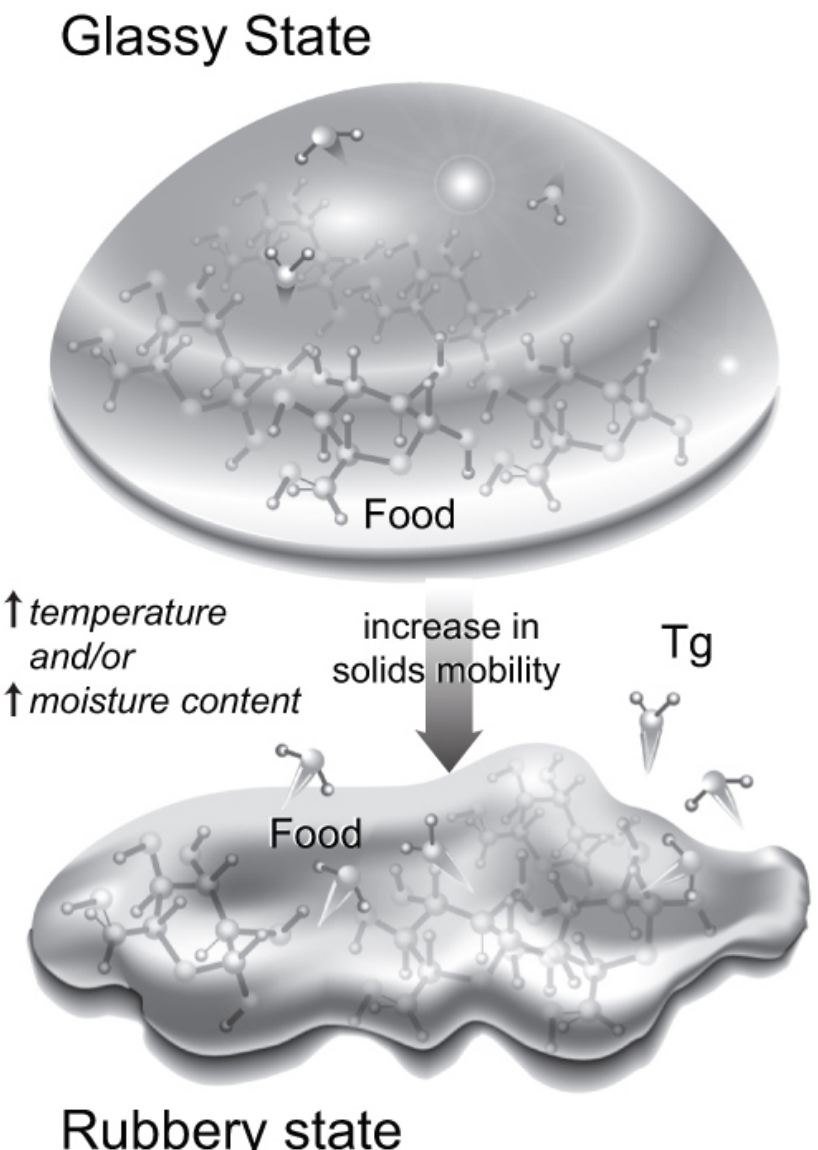
- Requires the use of expensive equipment and a high level of operator training and expertise

- Results require careful interpretation and are nuclei dependent

- Not very useful for solving problems that require quick solutions

Fundamental Principles

Glass Transition Temperature (Tg): The temperature at which an amorphous glassy material softens (becomes rubbery or viscous) due to the onset of long-range coordinated molecular motion. Most applicable to low moisture and frozen food ingredients and systems.



Molecular to macroscopic distance scales of solids (short to long)

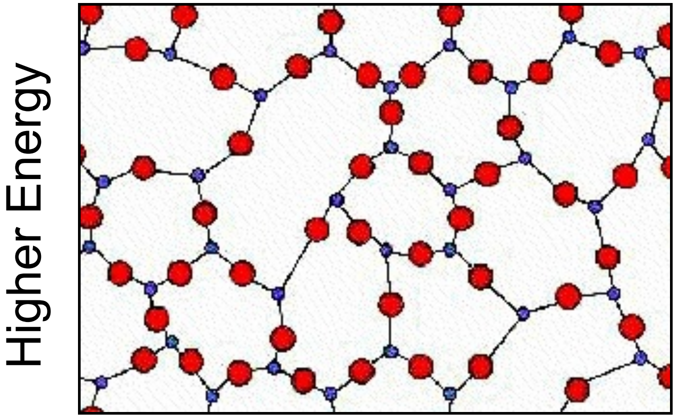
Polymer Science Approach

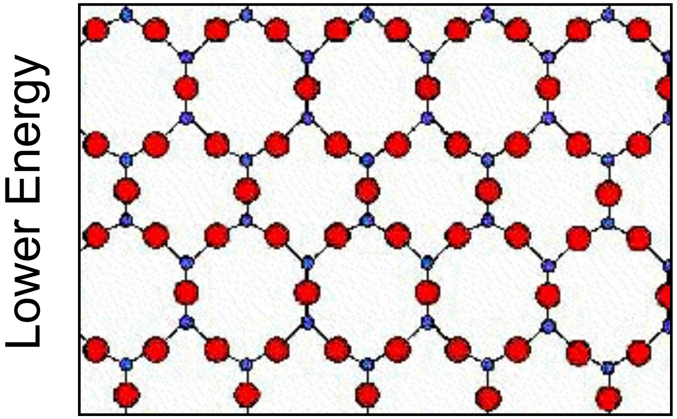
Examples of Amorphous Containing Food Materials

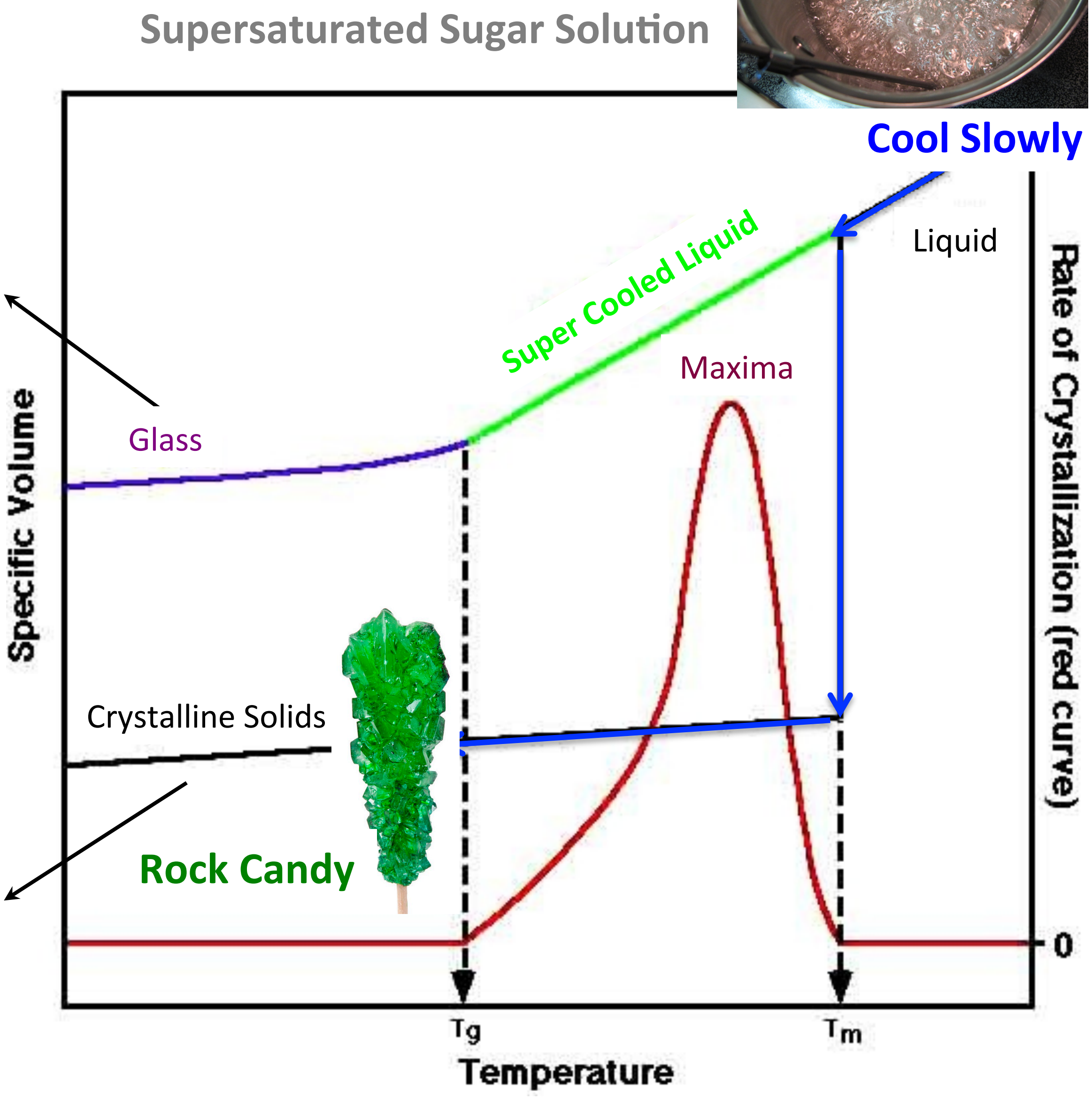
Method	Example Solid Systems	Amorphous Components
	Low Moisture (Tg)	**Contains Unfreezable water**
Rapid cooling and/or water removal	Spray-dried flavors	Carbohydrate carriers
	Milk powder	Lactose, Proteins
	Freeze-dried foods	Carbohydrates, Proteins
	Hard candies	Sugars
	Cereals and snacks	Carbohydrates, Proteins
	Frozen Foods (Tg')	**Contains Freezable water**
Freezing	Popsicles	Sugars
	Ice cream	Sugars, Proteins
	Vegetables	Carbohydrates, Proteins

Polymer Science Approach

Fundamental Principles: Low Moisture Foods





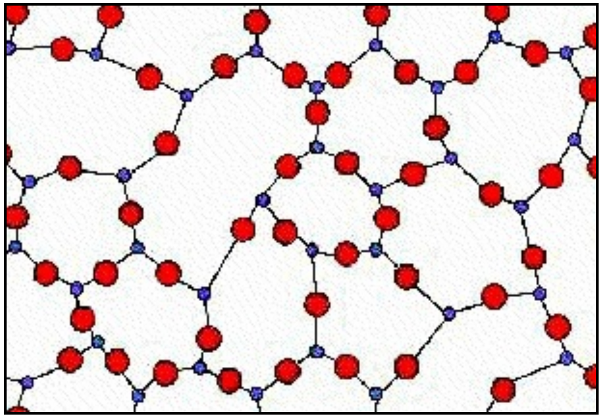


Polymer Science Approach

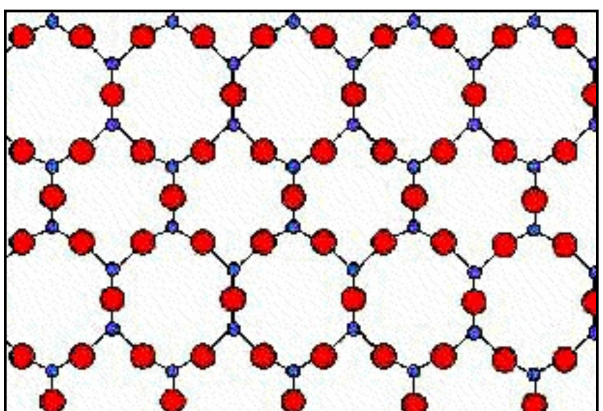
Fundamental Principles: Low Moisture Foods

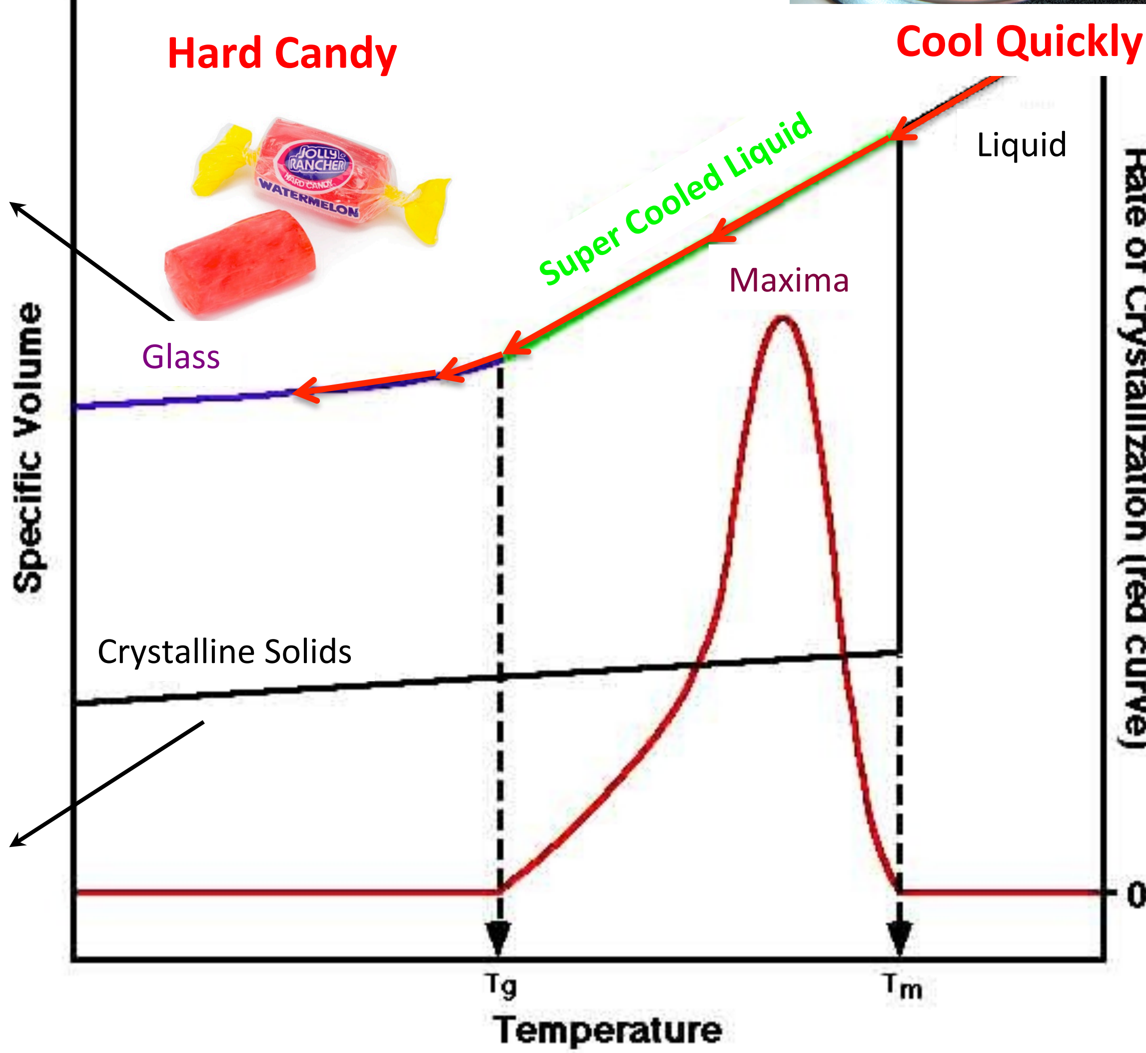
Supersaturated Sugar Solution

Higher Energy



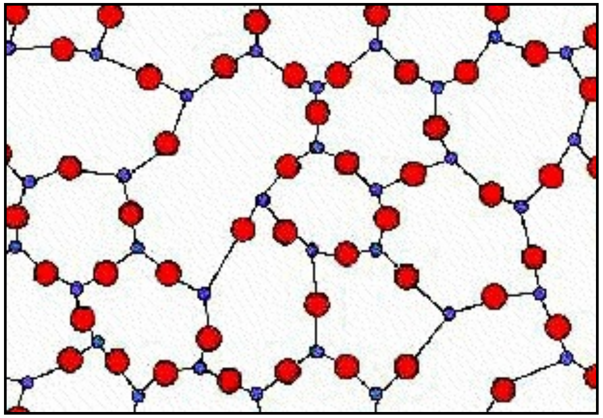
Lower Energy



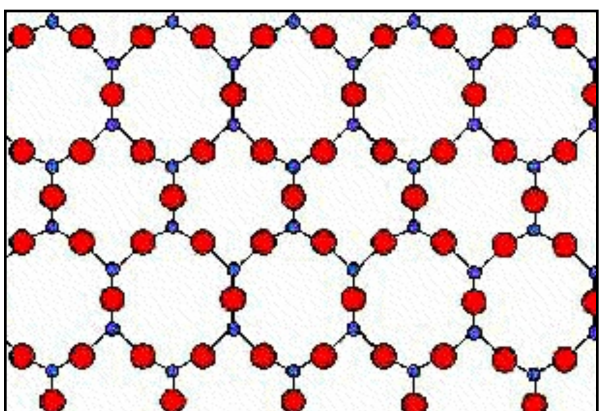


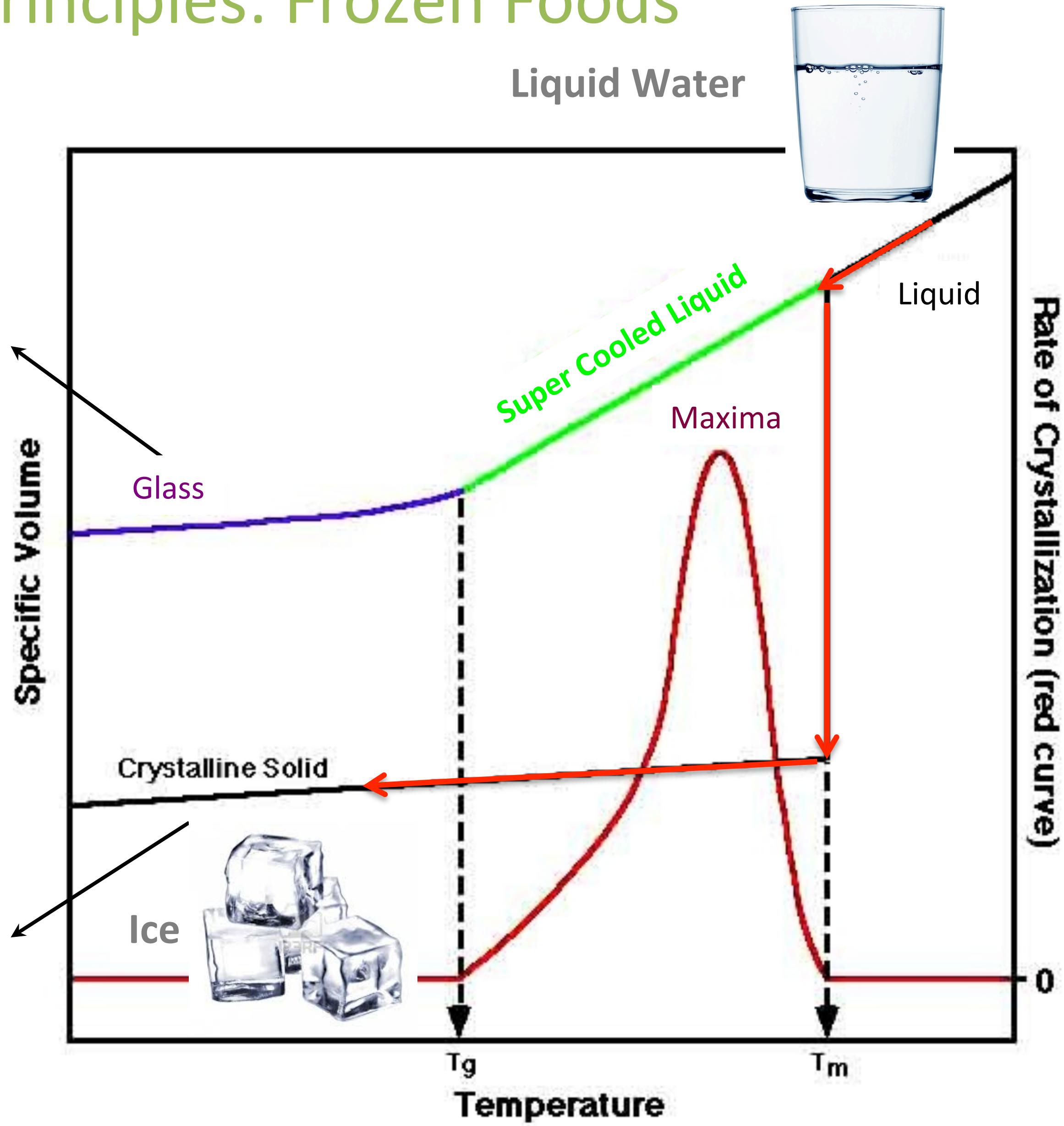
Fundamental Principles: Frozen Foods

Higher Energy



Lower Energy



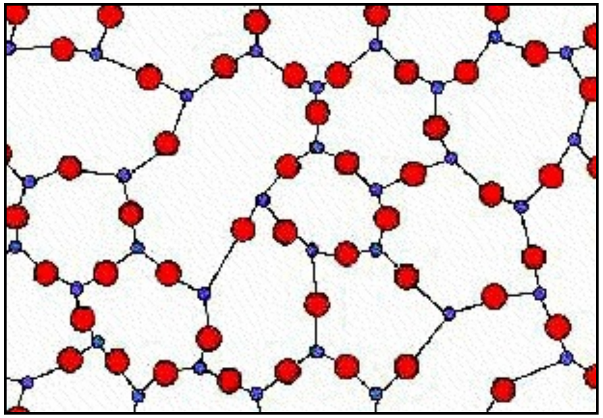


Polymer Science Approach

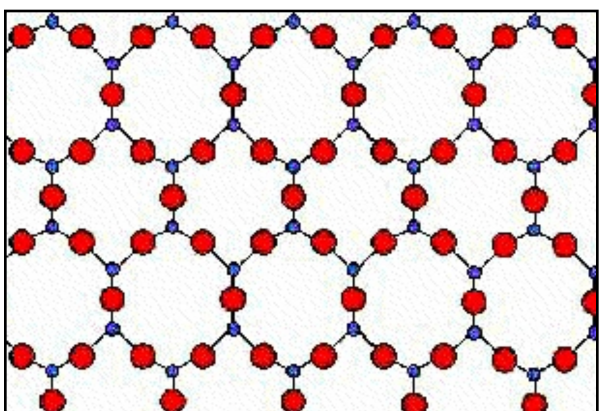
Fundamental Principles: Frozen Foods

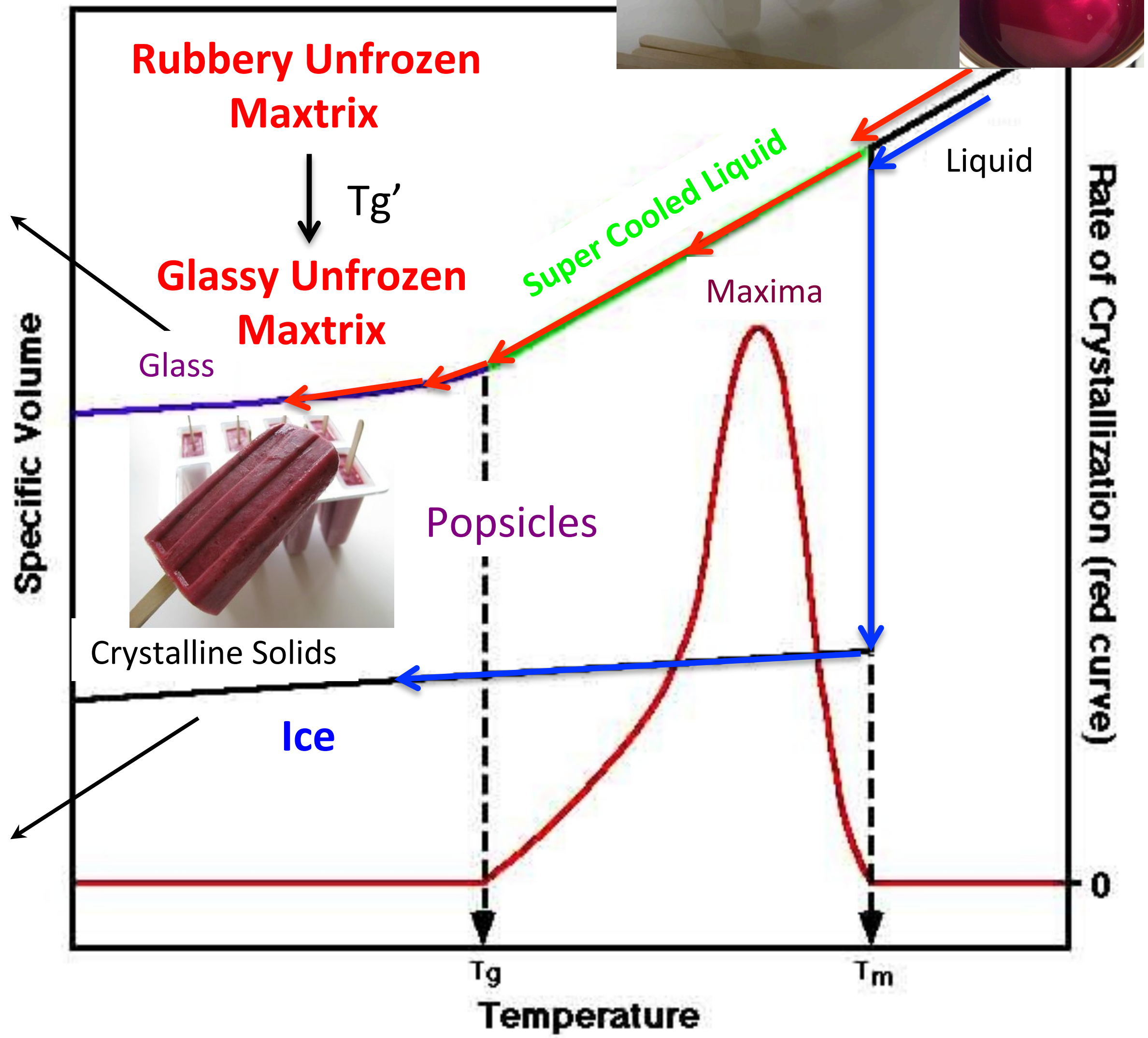
Sugar Solution with Flavor and Color

Higher Energy



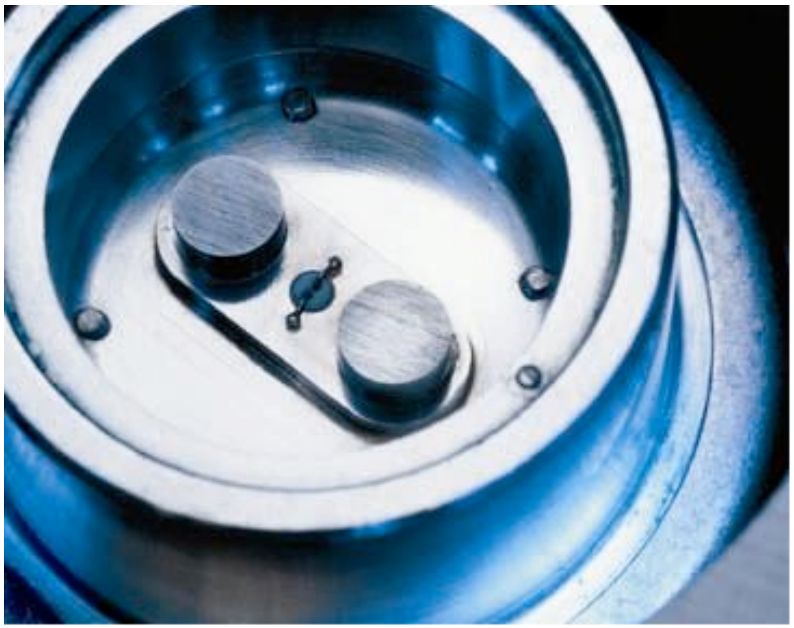
Lower Energy





Measurement Methods

Differential Scanning Calorimetry (DSC)



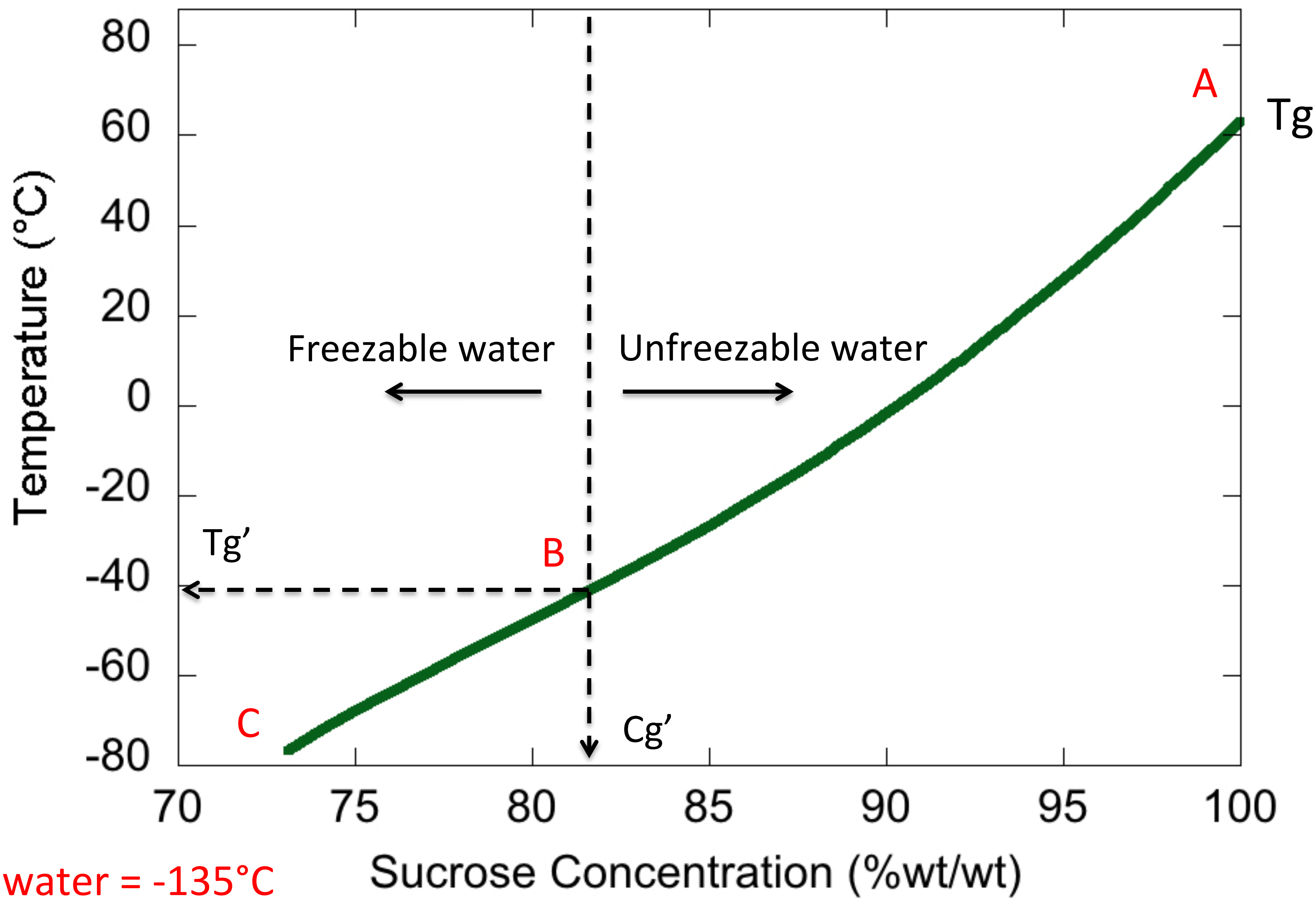
Many other methods, such as, Dynamic Mechanical Analysis (DMA), Dynamic Mechanical Thermal Analysis (DMTA), Dielectric Analysis (DEA), NMR, and ESR

Example DSC Tg and Tg' Values

Material	Tg midpoint (°C)	Tg'midpoint (°C)
Xylitol	-23	-67
Sorbitol	-4	-57
Fructose	10	-53
Glucose	36	-53
Maltitol	44	-42
Sucrose	67	-41
Raffinose	77	-32
Maltose	92	-37
Trehalose	107	-35
Native starch (calculated)	243	

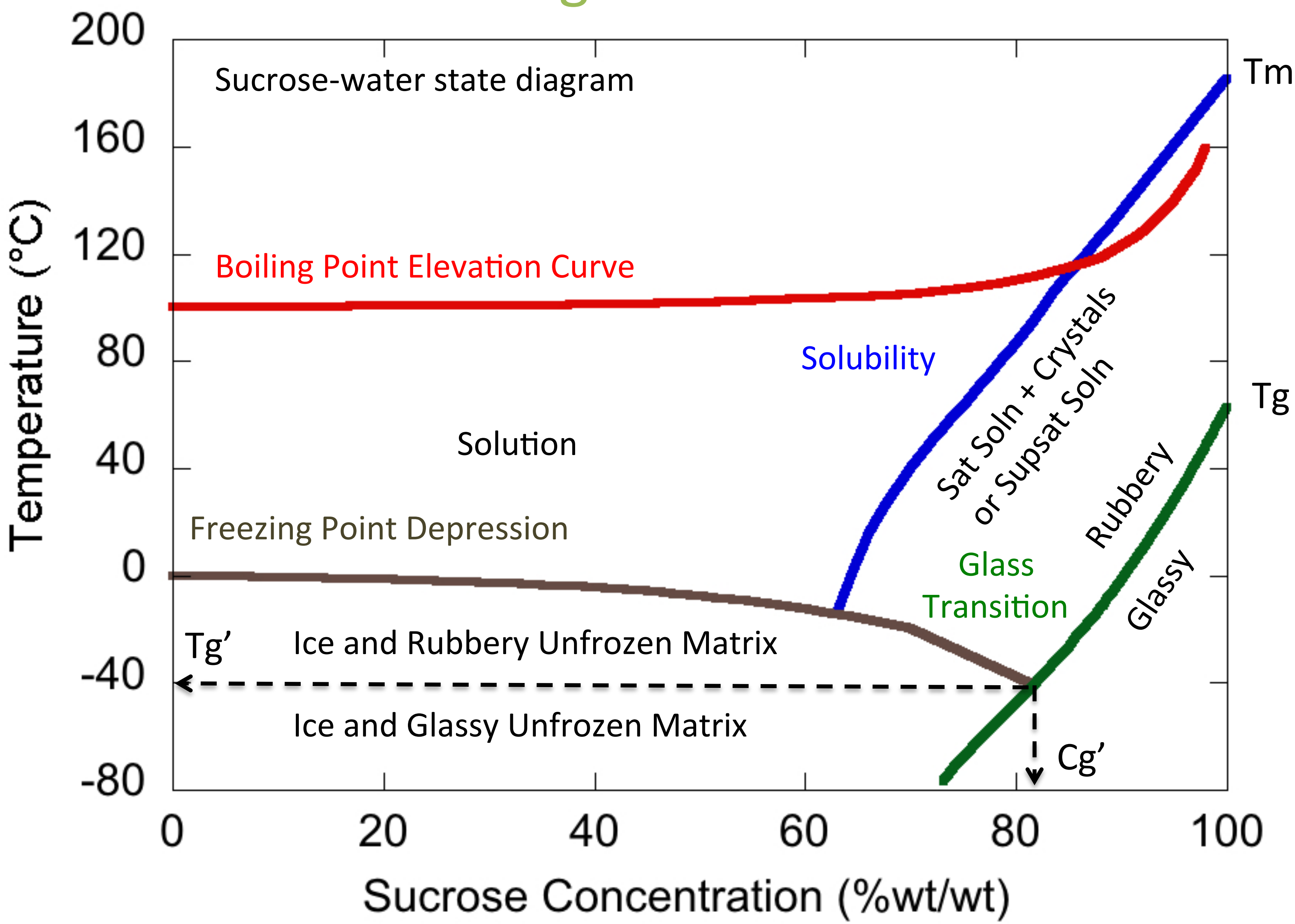
Polymer Science Approach

Tg Diagram: Sucrose



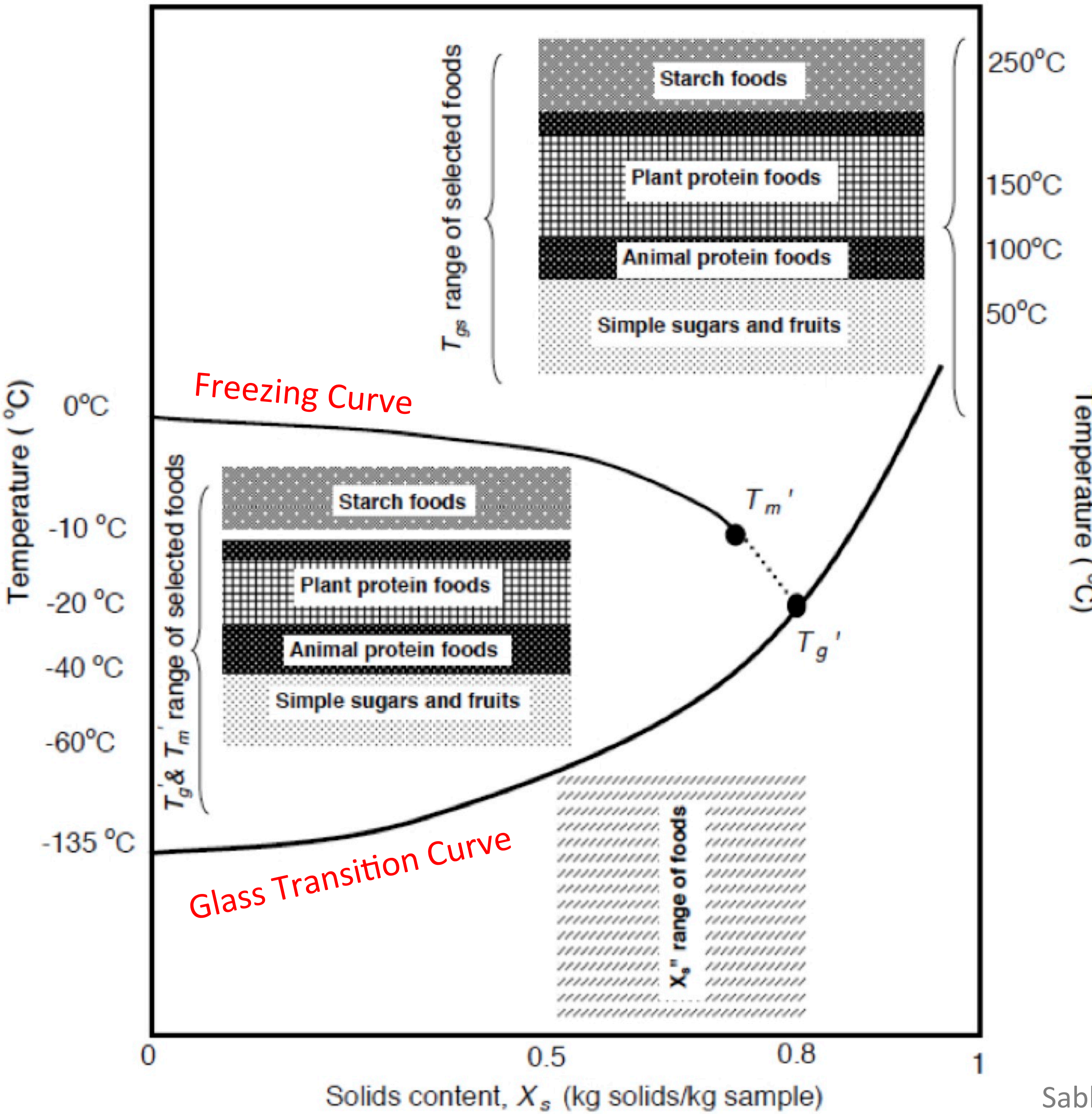
Tg water = -135°C

State Diagrams: Sucrose



Polymer Science Approach

Tg and Tg’ for Various Food Materials



Sablani and others 2010

Strengths and Limitations

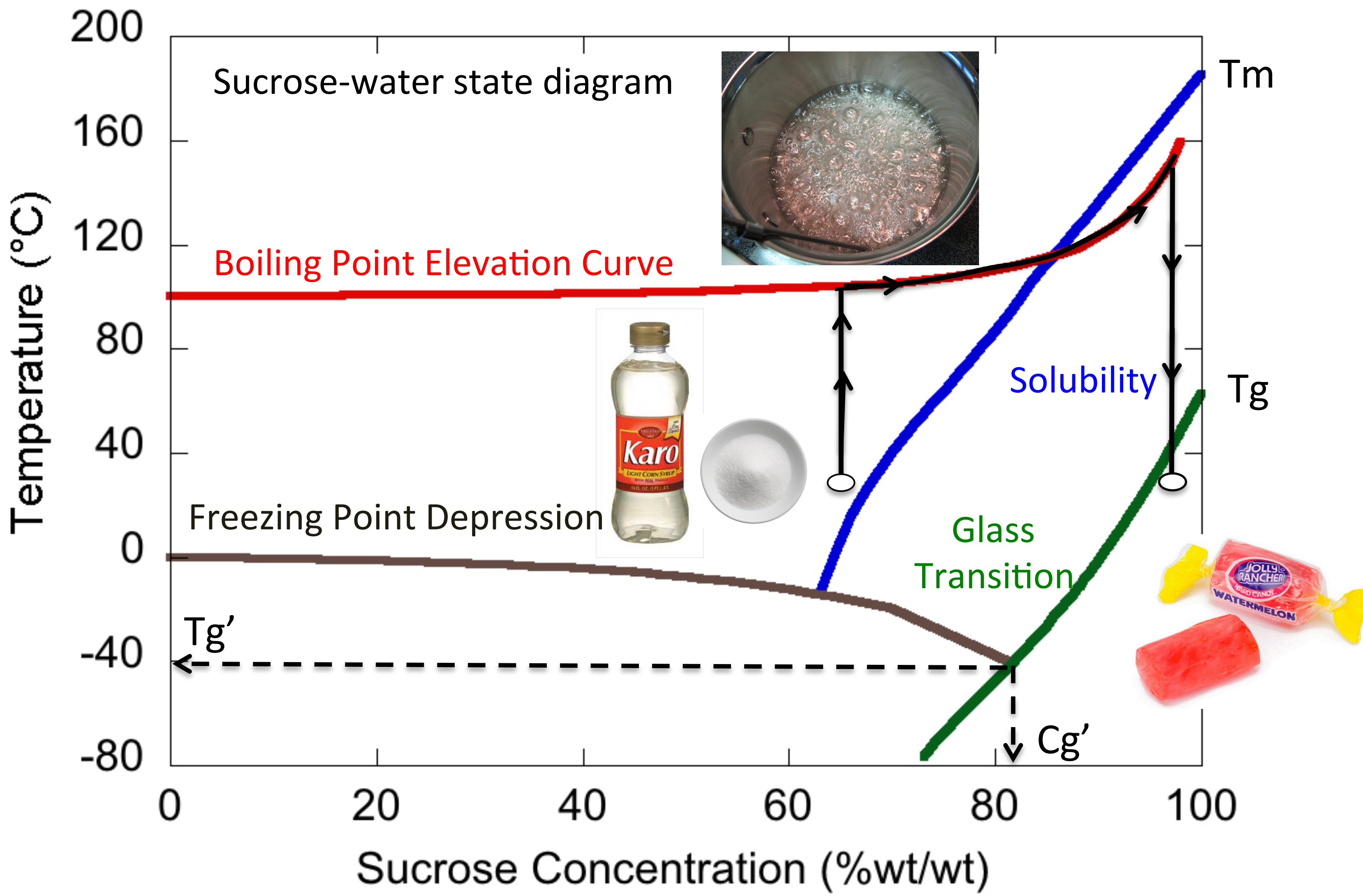
Strengths

- Kinetic approach that uses Tg as a physicochemical parameter that provides insight into processibility, product properties, quality, and stability of food systems
- Useful for formulating and predicting the stability of frozen food systems and the textural stability of low moisture systems

Strengths and Limitations

Strengths (con’t)

- State diagrams are very useful for mapping food processes and predicting product stability



Strengths and Limitations

Limitations

- Tg is measured as an average value for the amorphous system solids and is not uniquely measurable, but is method and parameter dependent
- Tg has not shown consistent correlation to microbial stability or reactions that are not diffusion limited
- Currently there is no routinely applied method that can be used to measure the Tg of real foods, but dynamic isotherm research is on going

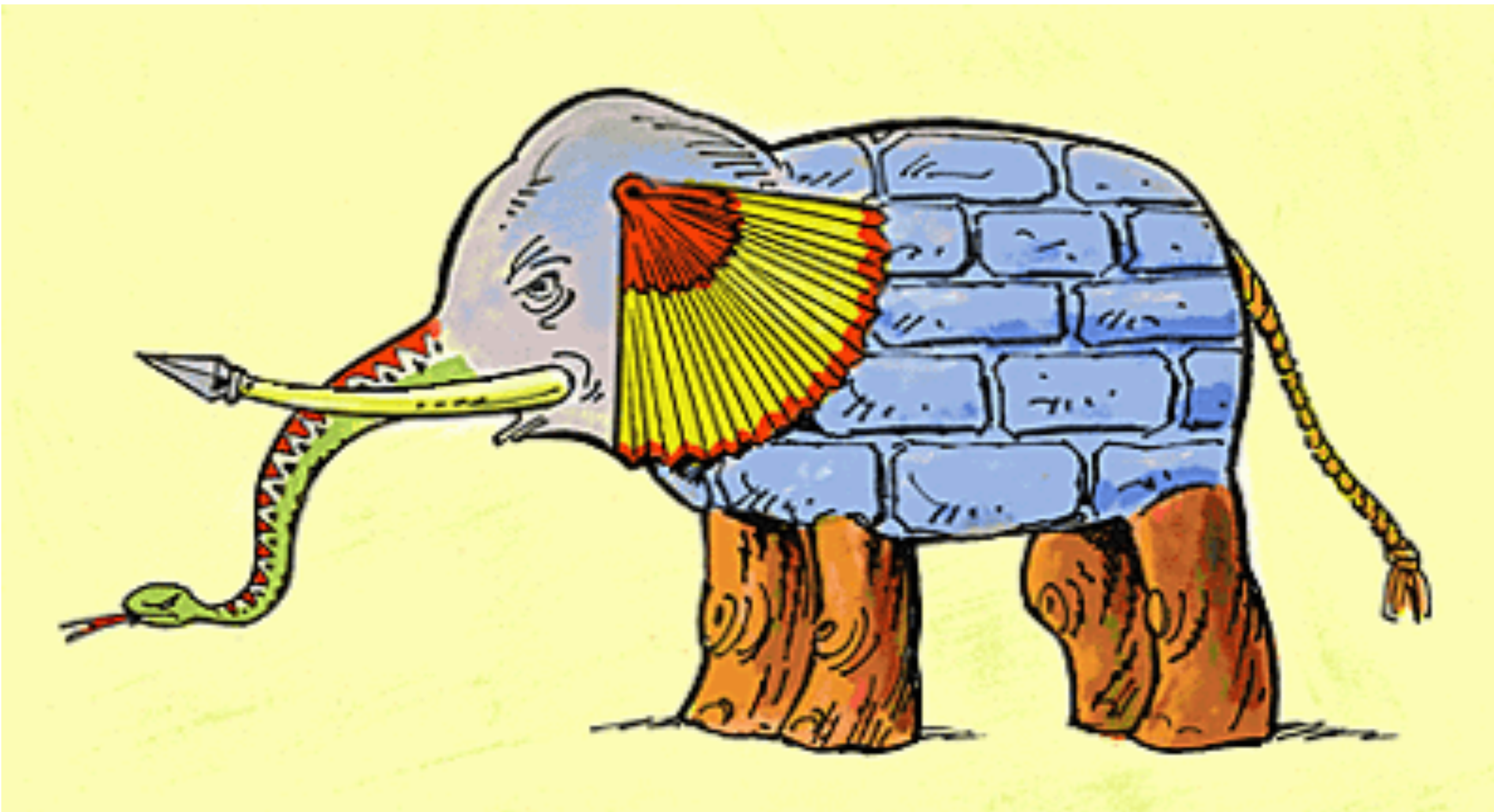



Q. Which approach is best to probe the stability of a food system?

A Brief Story…

The Moral of the Story…

All of the men were individually correct, but the best picture of the elephant was obtained by putting all the parts together!



The Moral of the Story…con’t

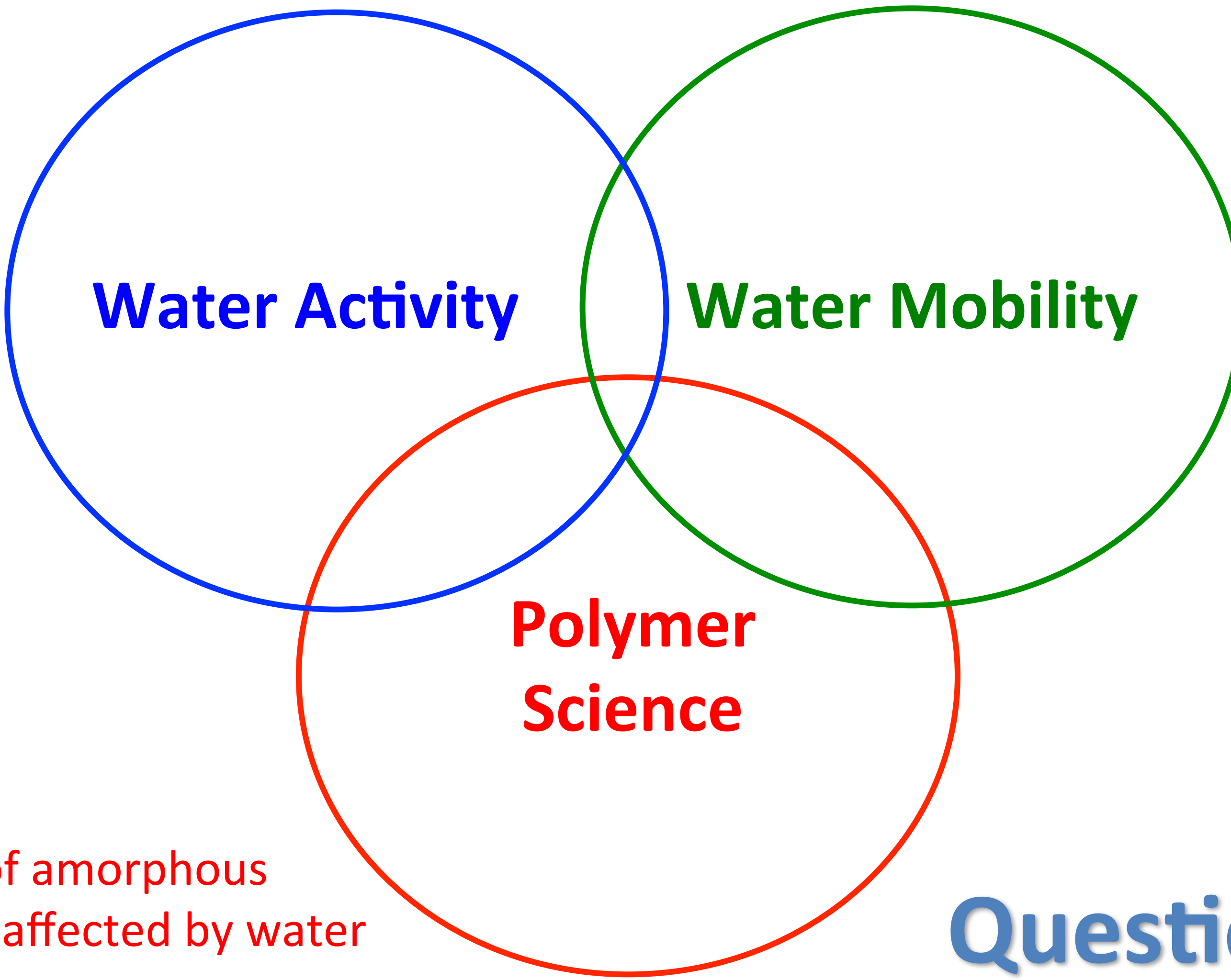
a_w, Water Mobility, and Polymer Science (Tg) are not competitive approaches to solving the same problem; rather these approaches are complementary and should be used in concert to obtain a composite, multi-level (at various distance and time scales) portrait of the water and solids dynamics that govern the stability behavior of a food system.

Thus, the “best” technique(s) to use depends on the problem being investigated.

A Combined Approach…

a_w: property of the water molecules outside the food as affected by solids

Water mobility: property of the water molecules inside the food as affected by solids



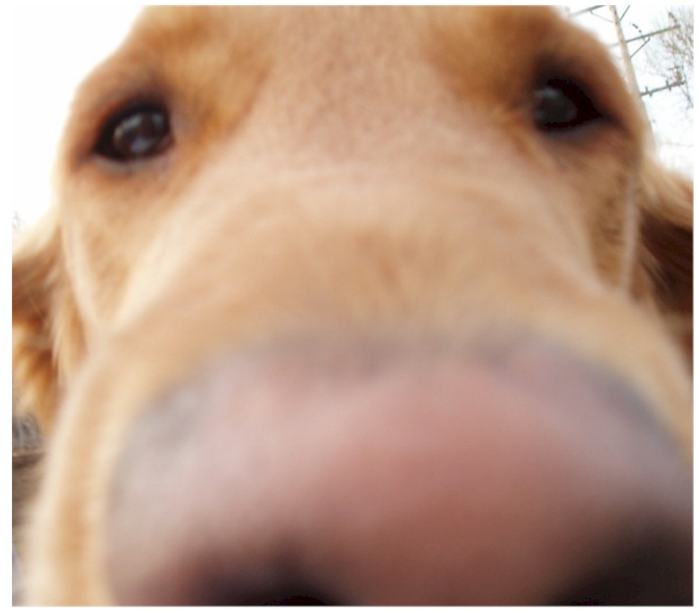
Tg: property of amorphous food solids as affected by water

Questions?

Case Study

What happened to the Tasty Chunks?

The IMF pet food arrived to its destination via railroad car. A very strong sour off odor was detected upon its arrival. Microbial tests show no significant viable microorganisms in the product. QC records show a safe a_w of 0.80 at 23°C when the product left the manufacturing facility. What might have happened?



I Scream for Ice Cream!!!

You work for Frozen Treats-R-US Company. A new formulation was just developed and released that replaced half of the sucrose with xylitol and the artificial sweetener sucralose to create a low sugar, low calorie product. However, there has been a significant number of customer complaints that the ice cream is developing a grainy texture more quickly compared to the sucrose-only formula. Can you explain why this might be occurring?

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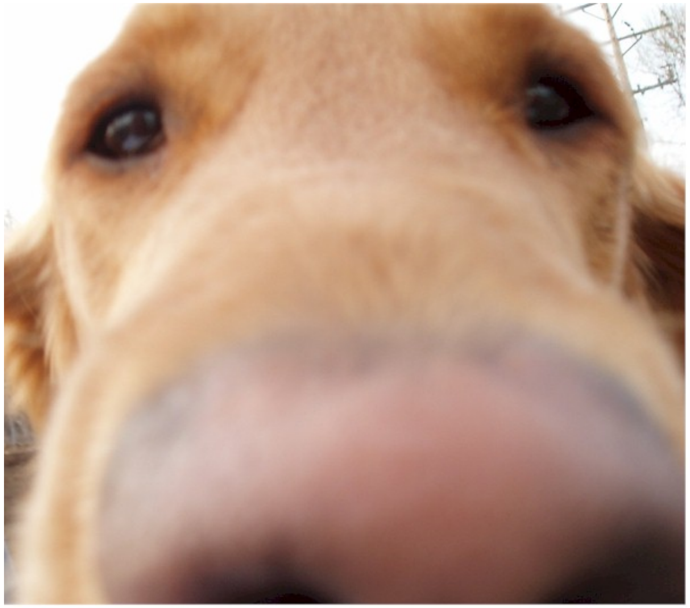
Case Study

What happened to the Tasty Chunks?

The high temperatures in the railroad car (~45°C) caused an increase in a_w and allowed microorganisms to grow (e.g., Lactobacillus), which produced acid and the sour off odor. Using the Clausius-Clapeyron equation, with a ΔH_{st} of 1,250 cal/mole for the pet food, aw is estimated to increase to 0.93 at 45°C.



Case Study

I Scream for Ice Cream!!!

Adding xylitol to the formula to replace half of the sucrose caused a decrease in the ice cream Tg', since the Tg' of xylitol (-67°C) is significantly lower than for sucrose (-41°C). At a standard freezer temperature of -18°C, the unfrozen matrix for both products is rubbery. However, the sucrose containing formula has a smaller ΔT than the xylitol one. A larger ΔT results in a more mobile unfrozen rubbery matrix, where both lactose and ice crystallization can occur at a faster rate.