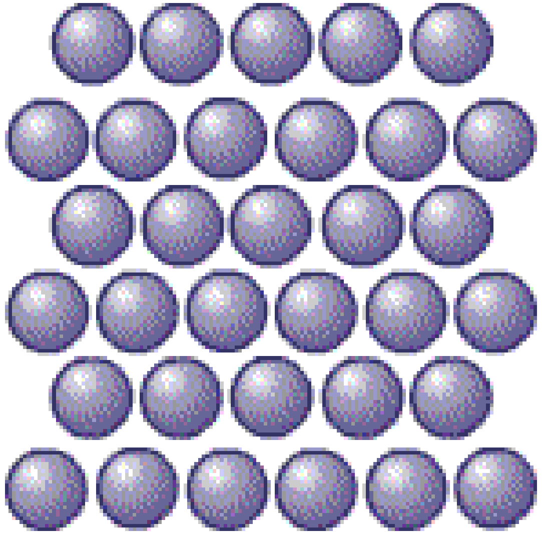
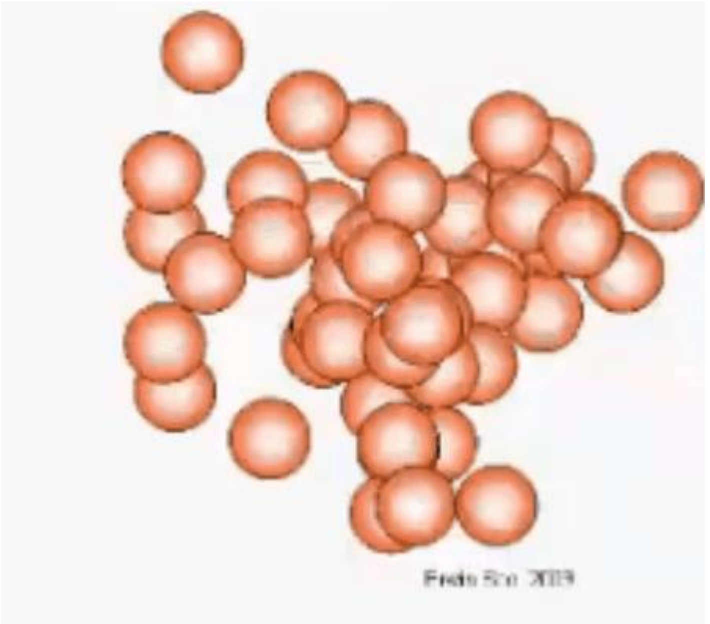
The Basics of Freezing: Thermodynamics and Kinetics in a Quiescent System



John Coupland

Penn State

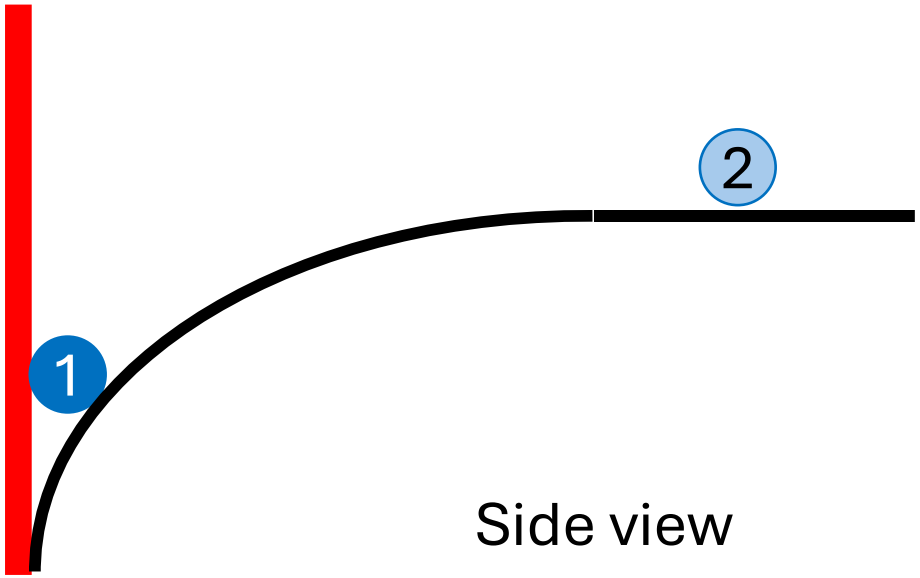


coupland@psu.edu

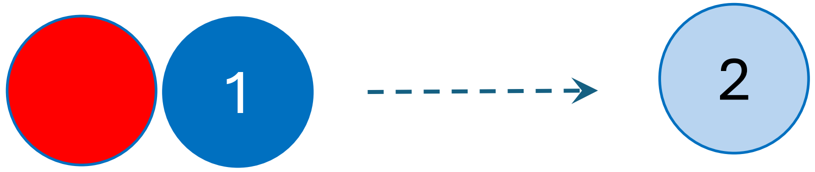
Gravitational Potential Energy Differences

Imagine a ball trapped in the bottom of a trench. What is the energy cost (ΔE) to move the blue ball from position 1 to 2? (or vice versa)?

Looking down from the top, what would be the forces felt by the blue ball at each position?



Side view

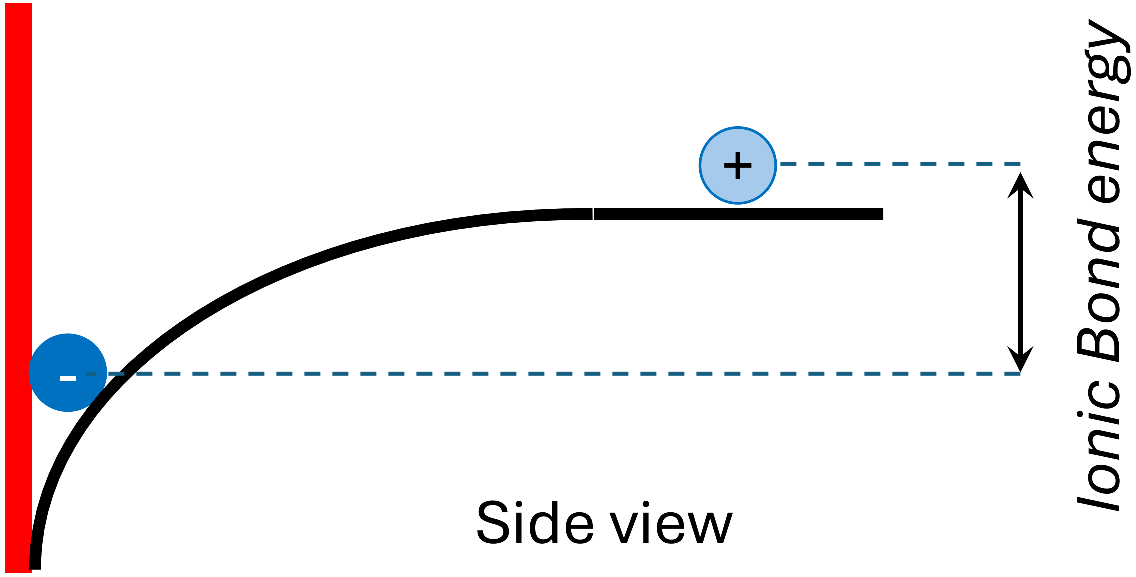


Top-down view

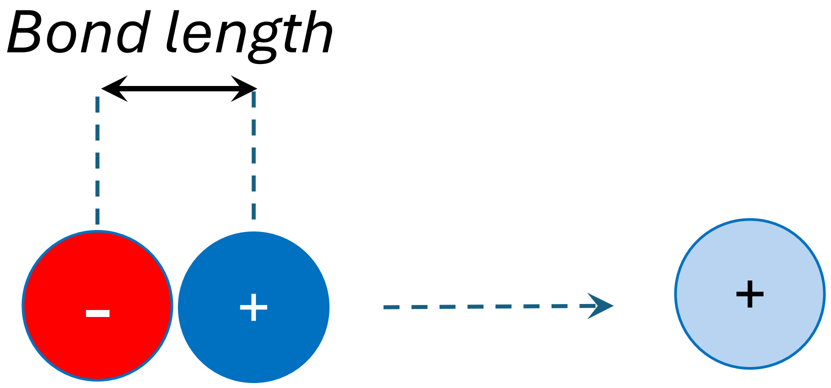
Electrostatic Potential Energy Differences

What is electrostatic potential energy we can infer from this?

Imagine two ions attracting one another. Fix the red ion; what are the forces on the blue ion?

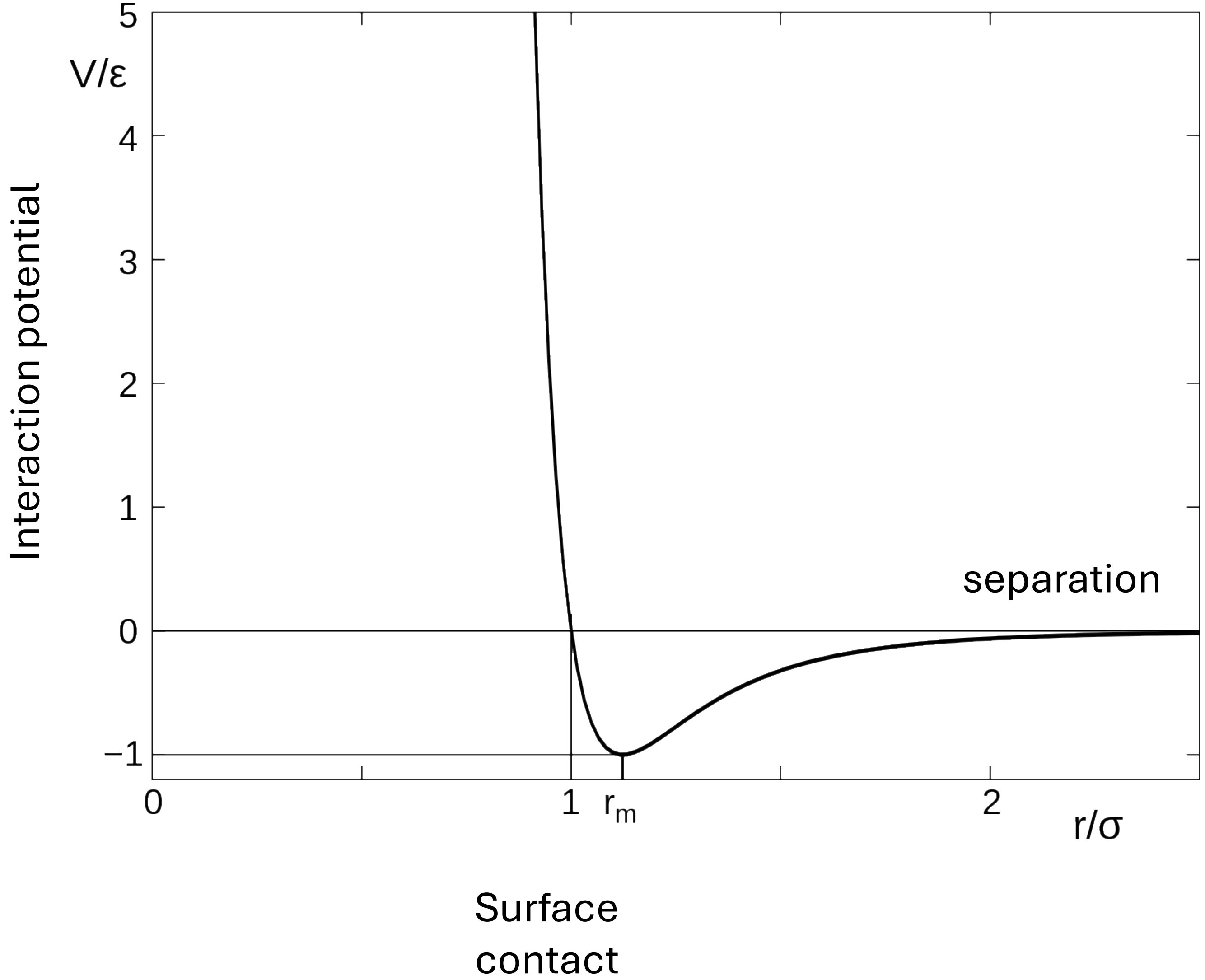


Side view

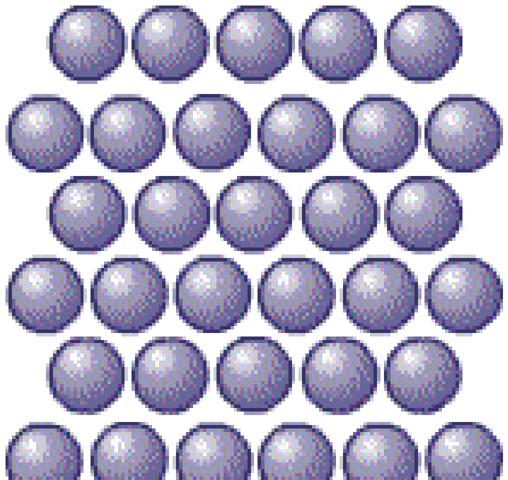


Top-down view

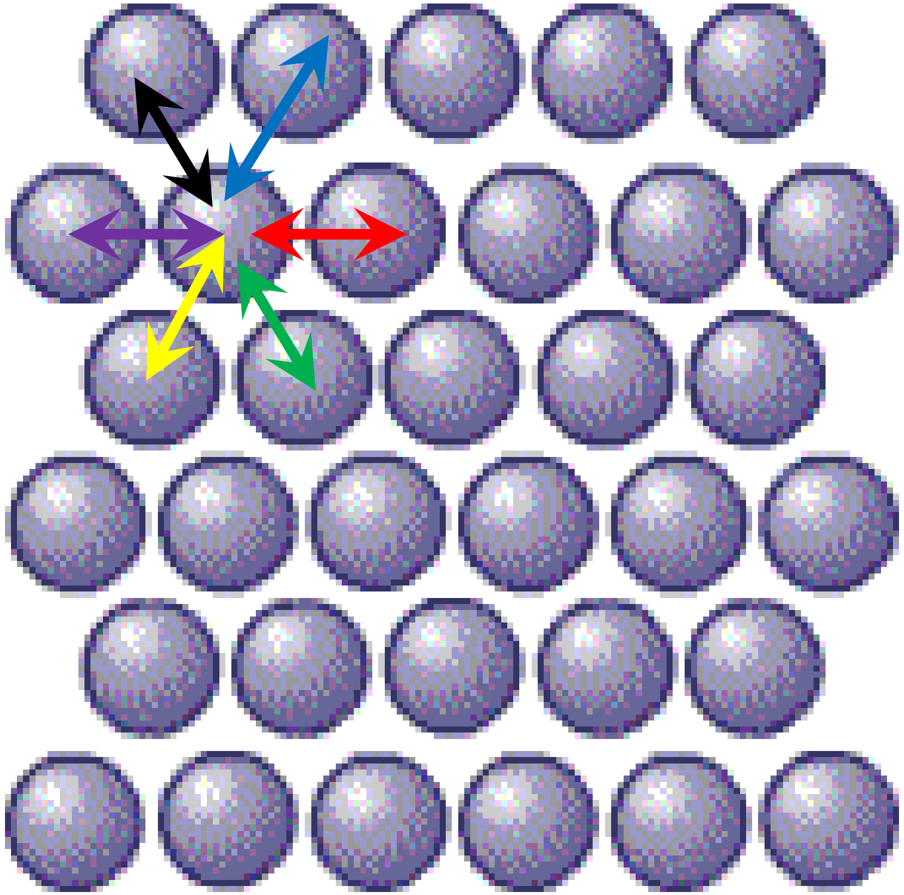
Intermolecular interactions

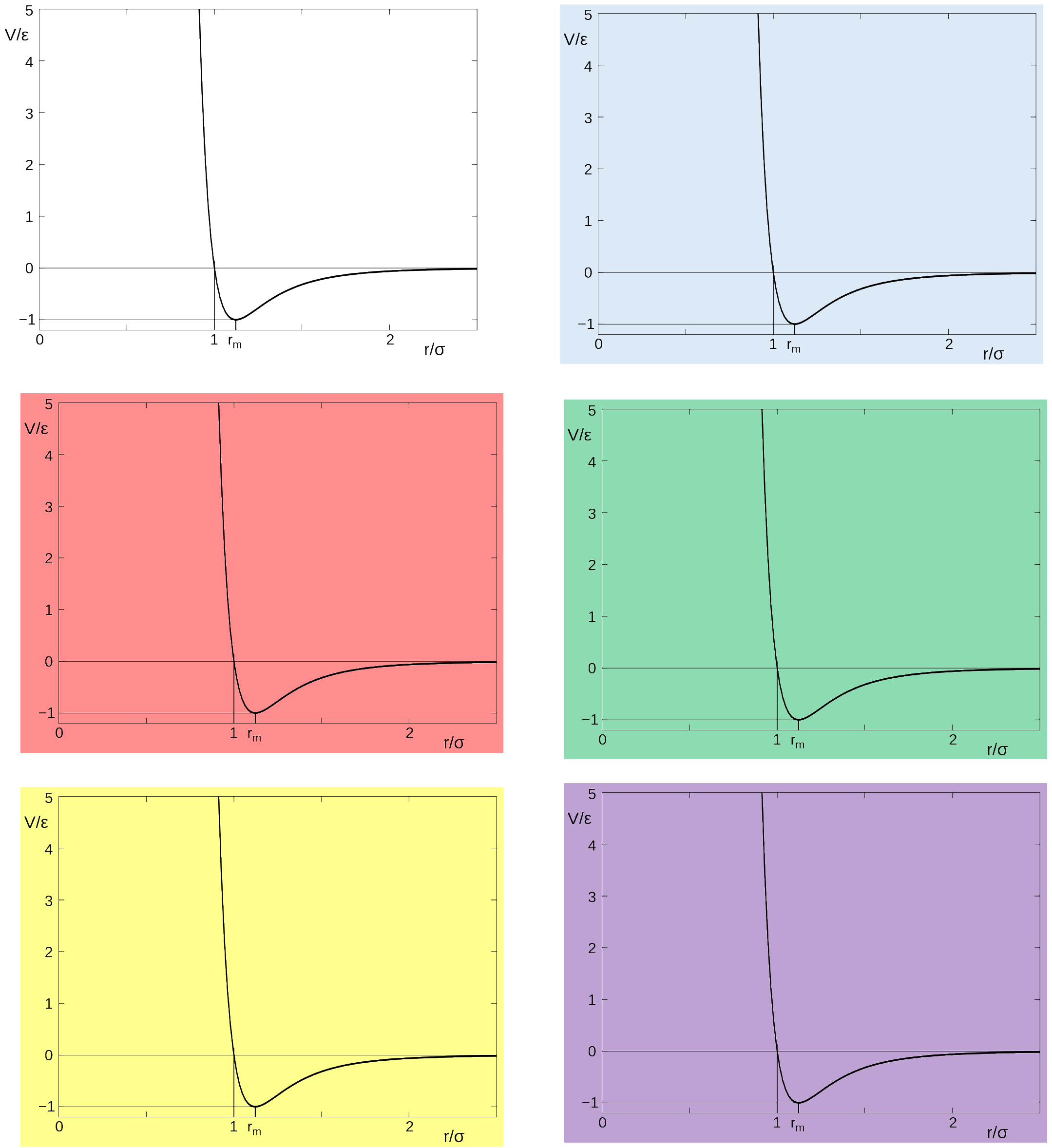


- Real intermolecular bonding potentials are more complex and depend on the details of chemistry
- In most cases we can assume a weak attraction at long ranges and a strong repulsion at short ranges
- In a crystal, most molecules oscillate around the resulting energy minimum



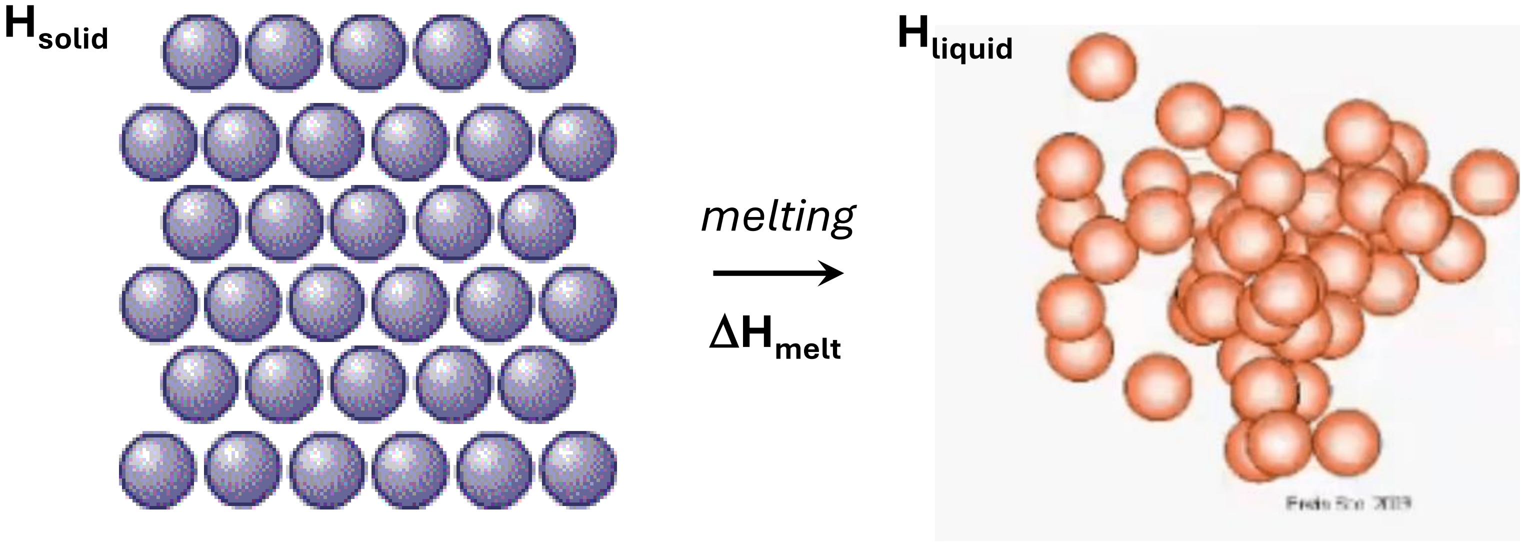
Internal energy is the sum of all the bonding potentials in a system





Internal energy ~ **Enthalpy** (H)

Change in Enthalpy (ΔH) – difference between two states



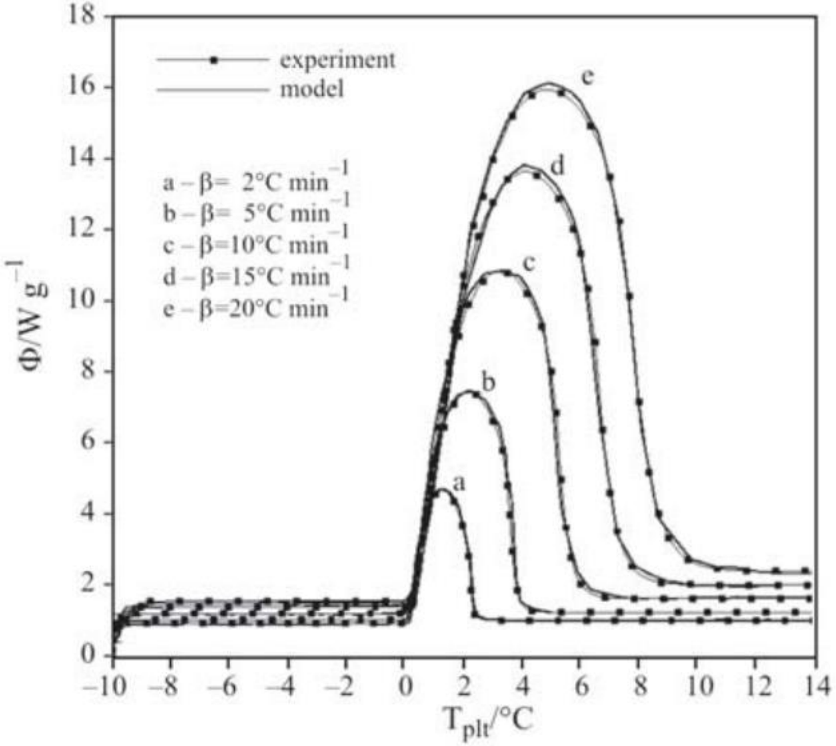
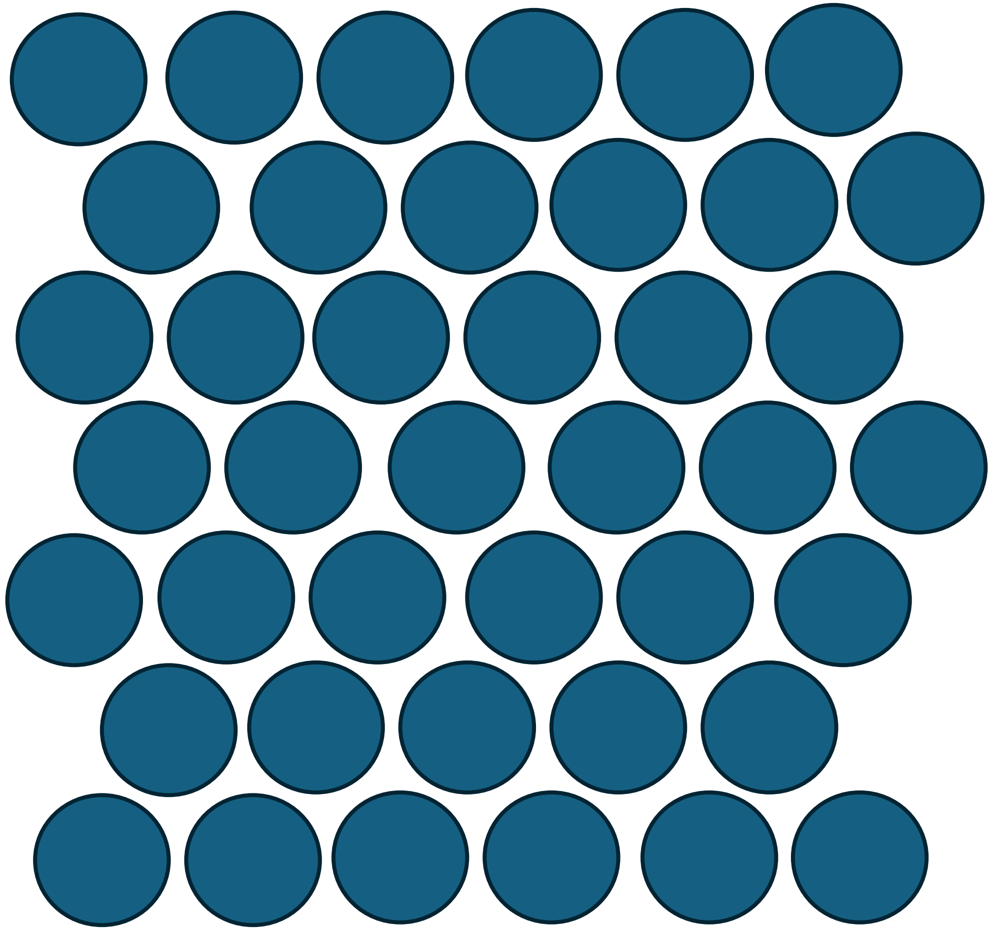


Fig. 4 Effect of the heating rate on the shape of curves

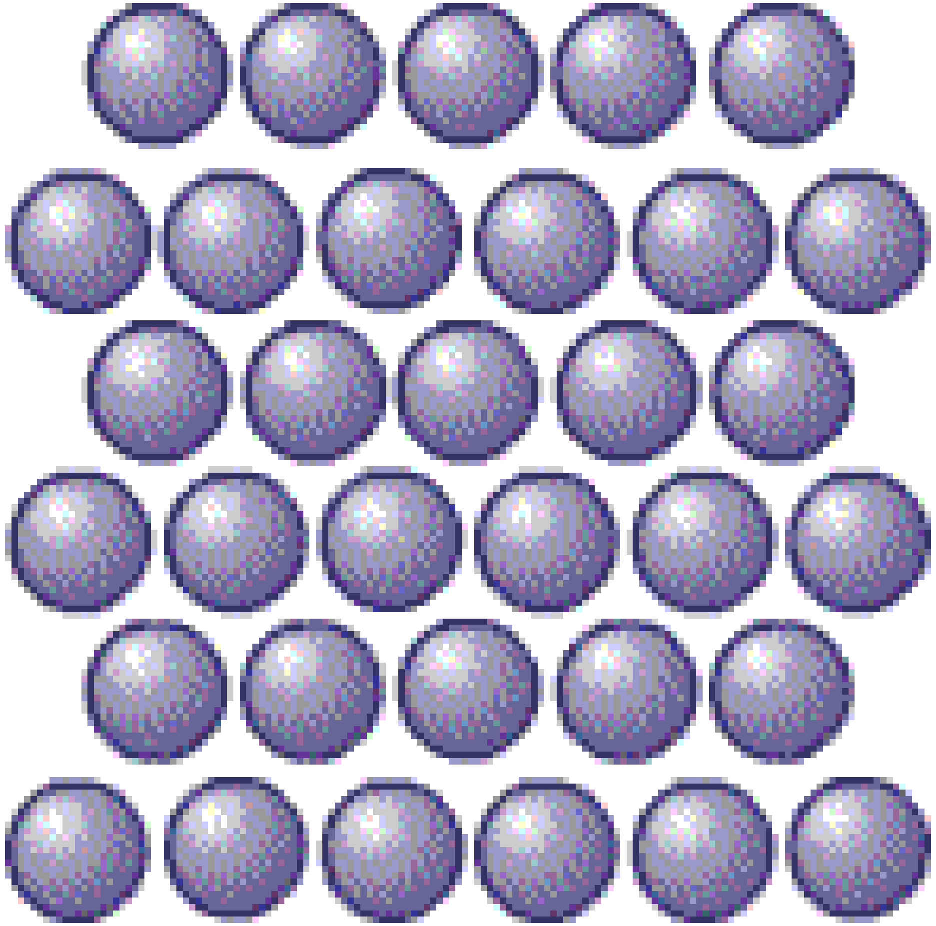
Enthalpy of the solid
Most atom pairs have their ideal separation (minimum on the potential energy function)

Enthalpy of the liquid
A variety of molecular separations, so each bond energy is higher (further away from the minimum)

Enthalpy of melting (ΔH_{melt})
The energy needed to move from one state to another. Put energy in to melt crystals (**endothermic**)



In our macroscopic world (ball rolling on a surface) we would expect everything to end up in its lowest energy position

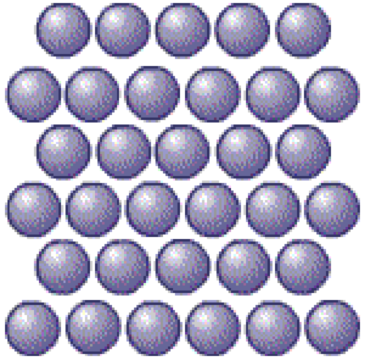


In a microscopic chemical system, we must account for the randomizing movements caused by heat

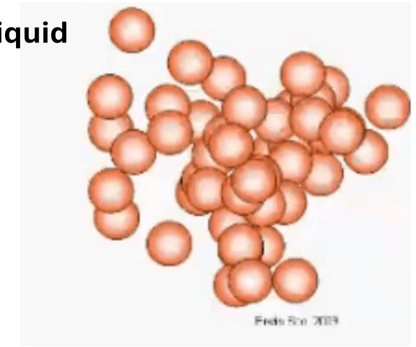
Entropy (S)

- Entropy increases with the number of microstates (ω or W)
- Microstates are “the number of ways the inside of a system can be arranged without changing the outside

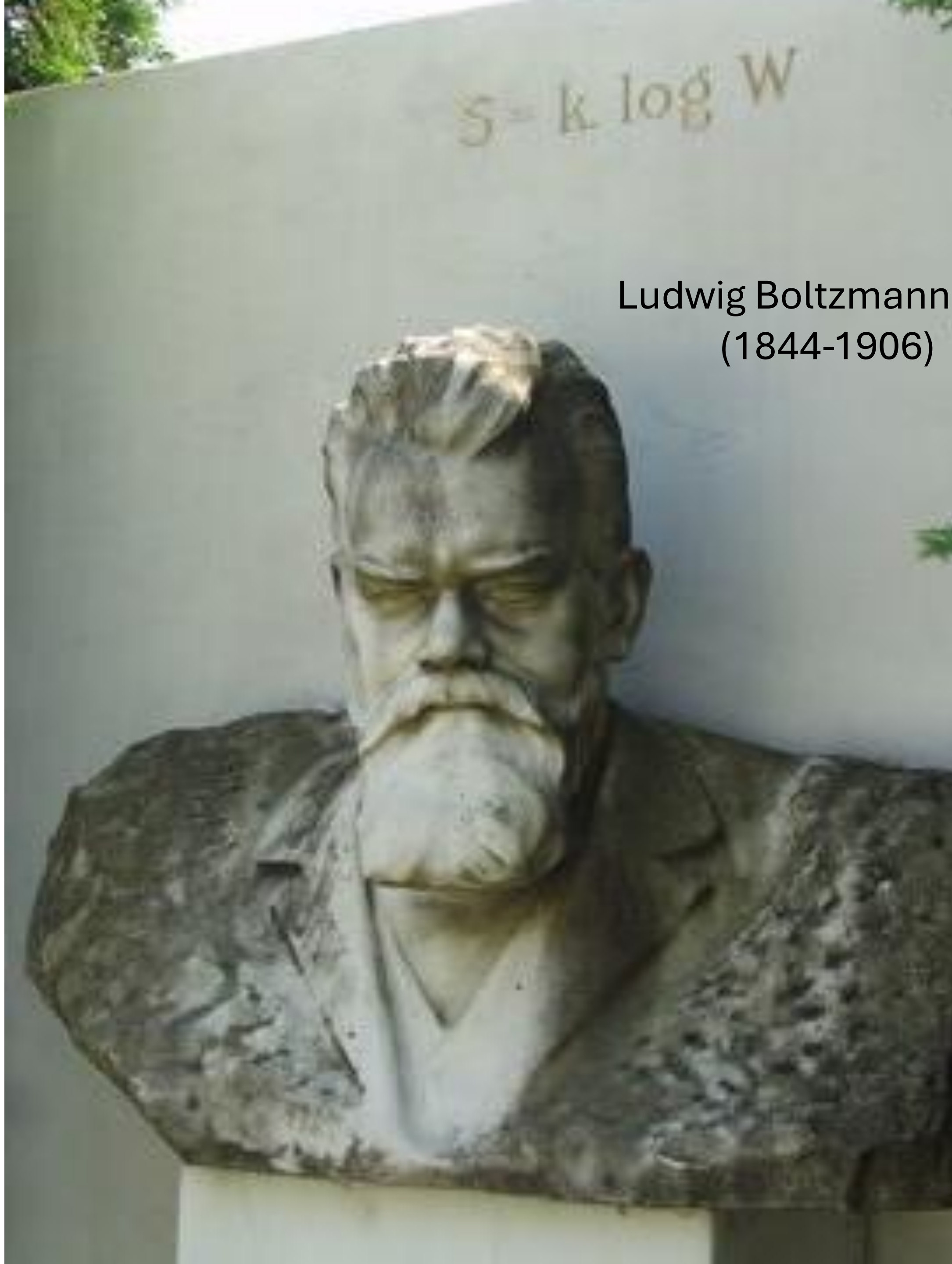
S_{solid}



S_{liquid}



- Solids have fewer microstates than solids (molecular positions fixed)
- The entropy of a solid (S_{solid}) is less than the entropy of a liquid (S_{liquid})



Ludwig Boltzmann
(1844-1906)

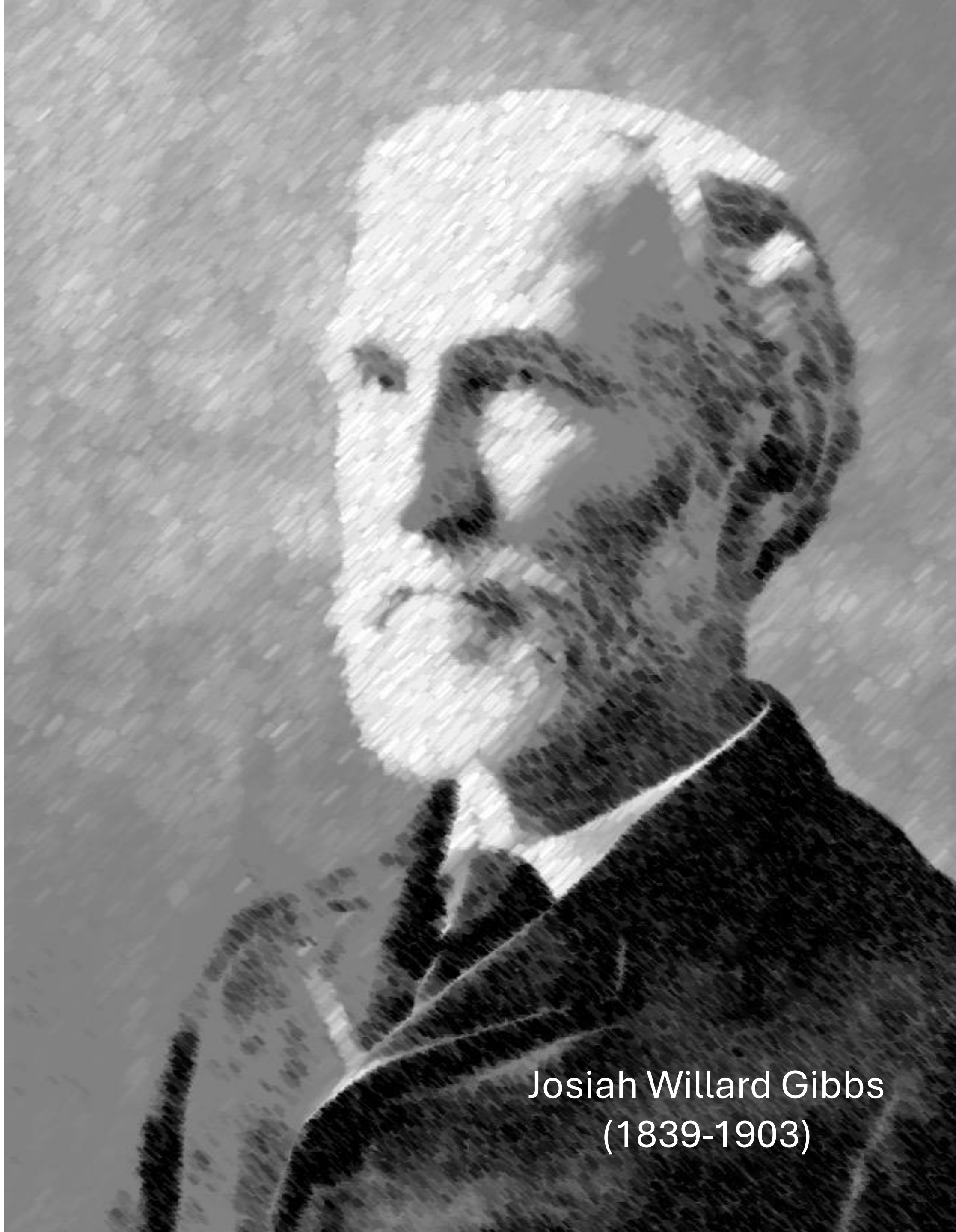
Gibbs Free Energy (G)

- The energy available to do external work. The enthalpy (total bond energy) minus a fraction for disordered, less useful energy:

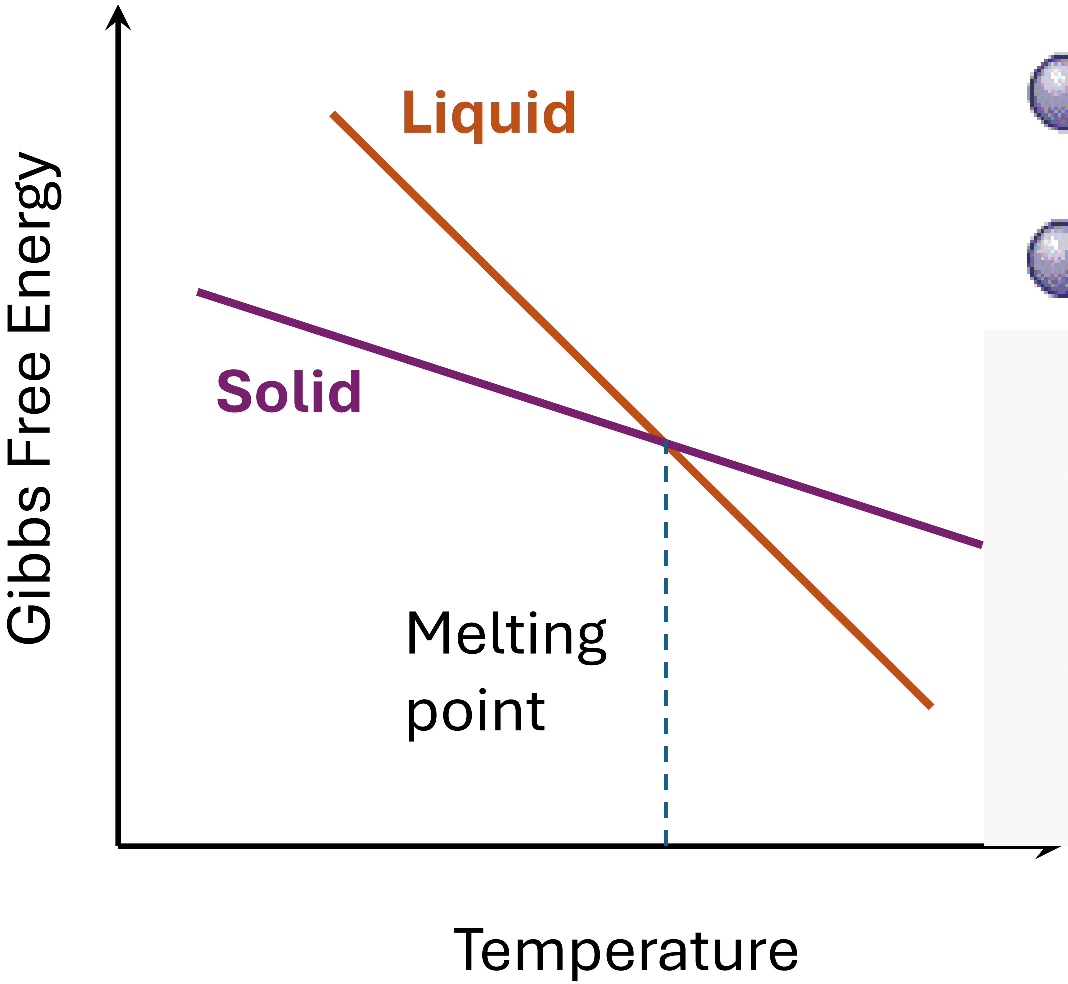
$$G=H-TS$$

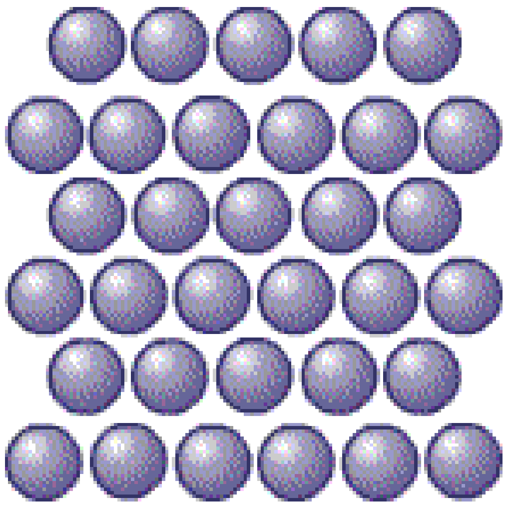
- For any change, the Gibbs free energy system must be negative:

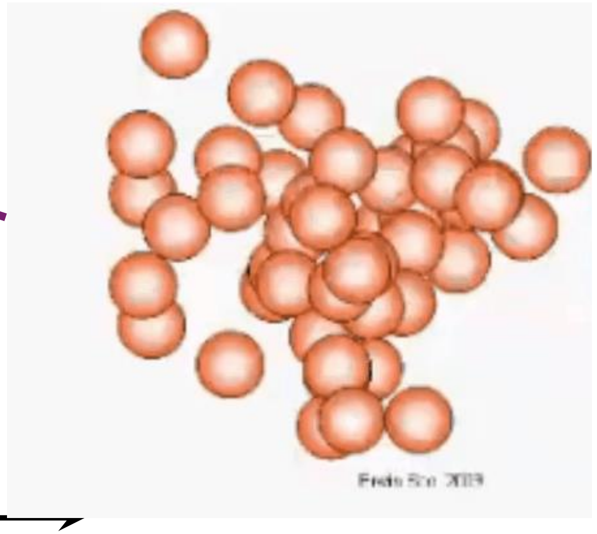
$$\Delta G = \Delta H - T\Delta S$$



G=H-TS







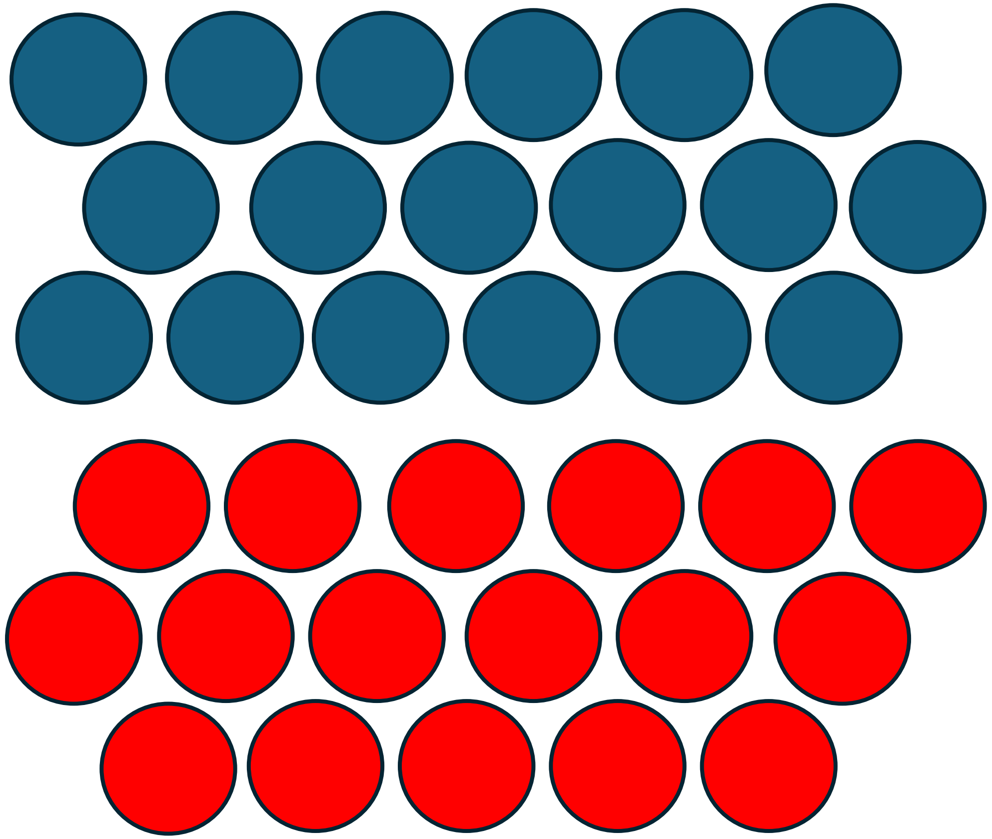
Solid

- Low enthalpy because better bonds
- G is small (when T=0 and G=H) -> lower intercept
- Lower entropy -> flatter slope

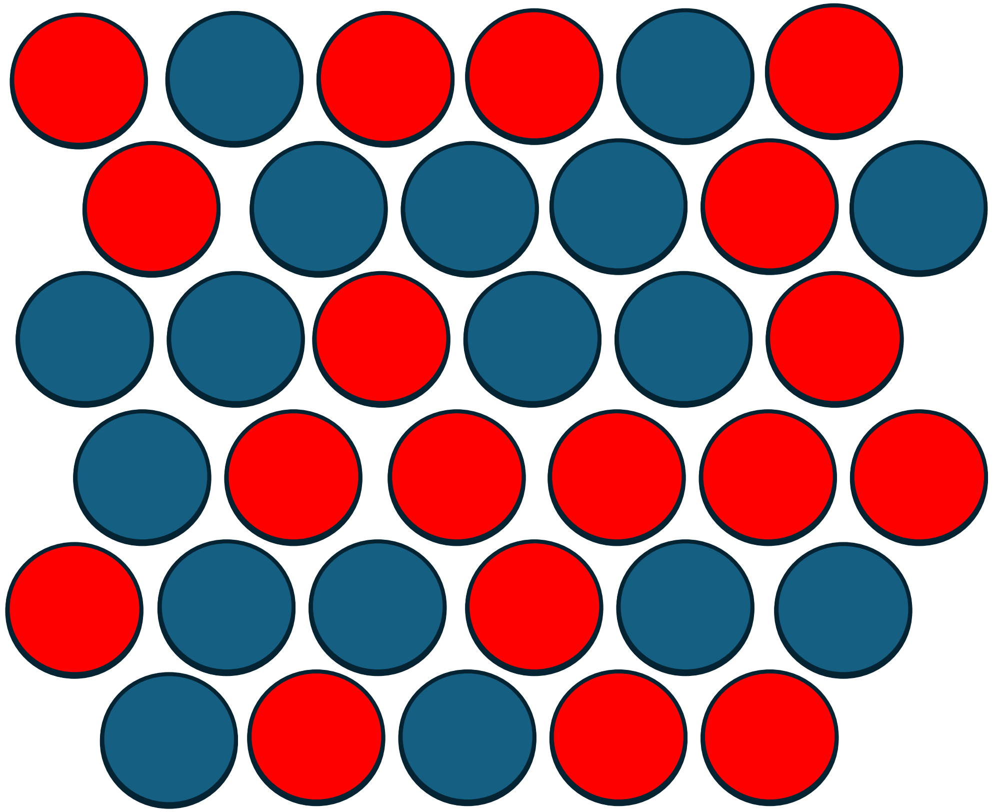
Liquid

- Higher enthalpy because worse bonds
- G is big (when T=0 and G=H) -> higher intercept
- Higher entropy -> steeper slope

Solutions have higher entropy than pure liquids

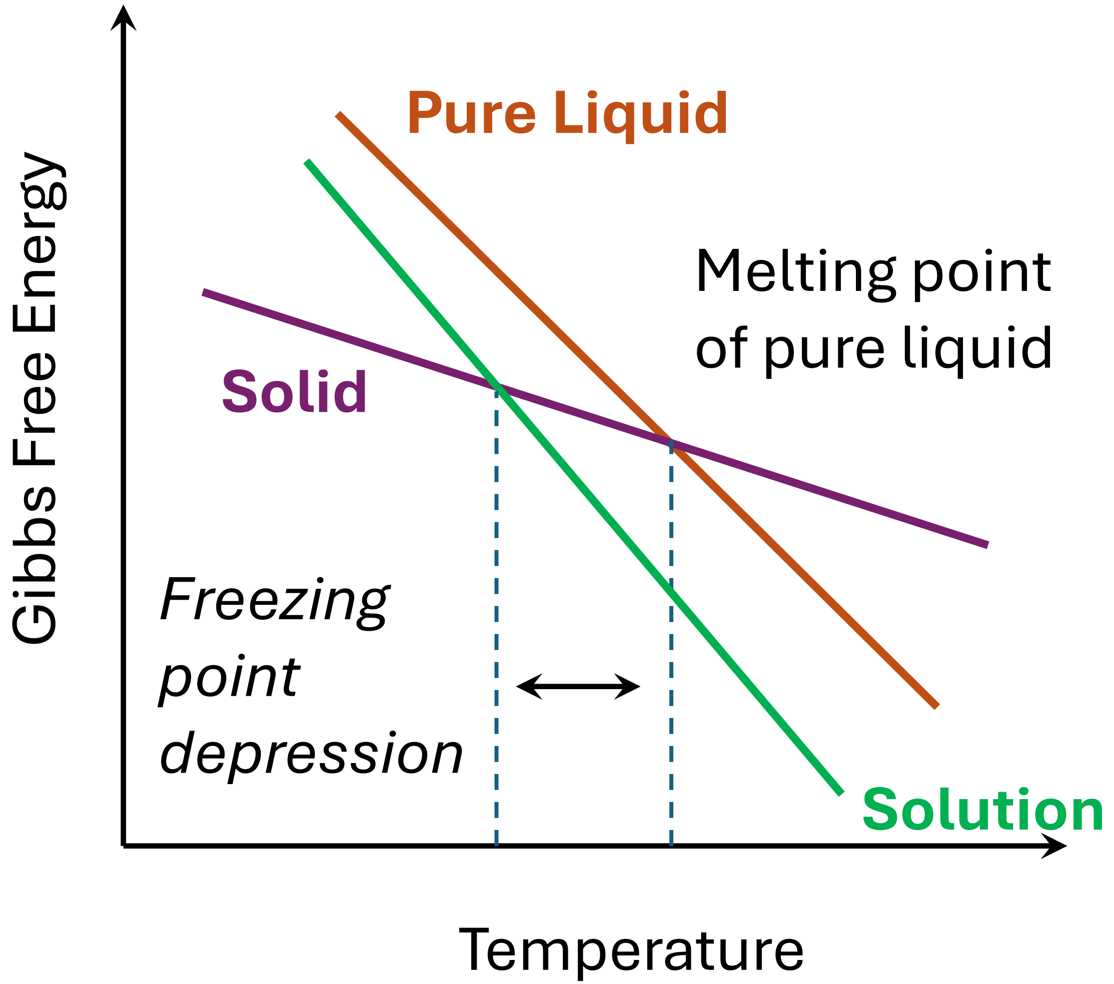


Moving molecules around in pure liquids doesn't create new microstates – all are effectively the same.



Mixing means many more microstates simply by molecules being in different positions. Mixtures have higher entropy

G=H-TS



Solid

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- G is small (when T=0 and G=H) -> lower intercept
- Lower entropy -> flatter slope

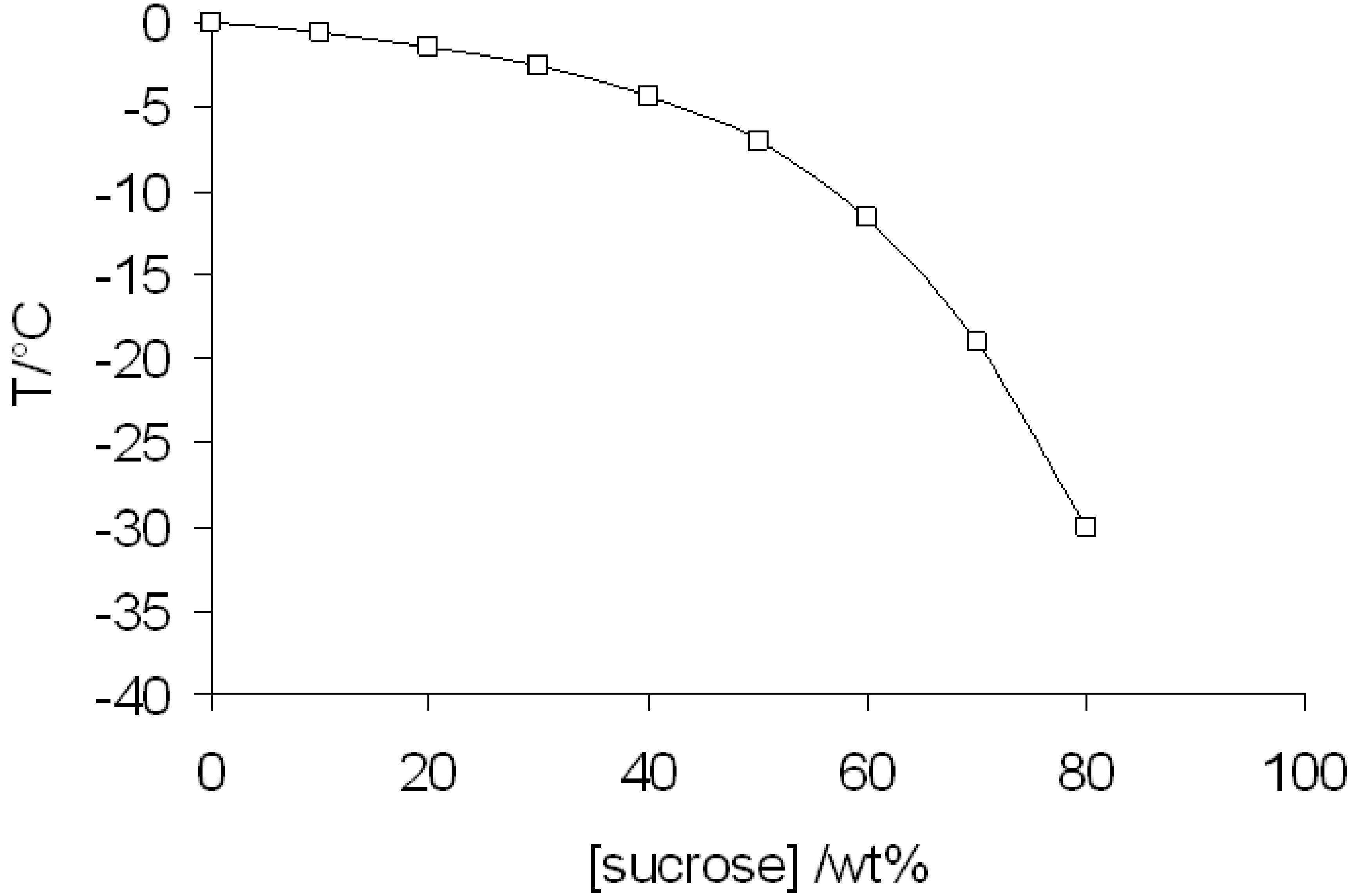
Liquid

- Higher enthalpy because worse bonds
- G is big (when T=0 and G=H) -> higher intercept
- Higher entropy -> steeper slope

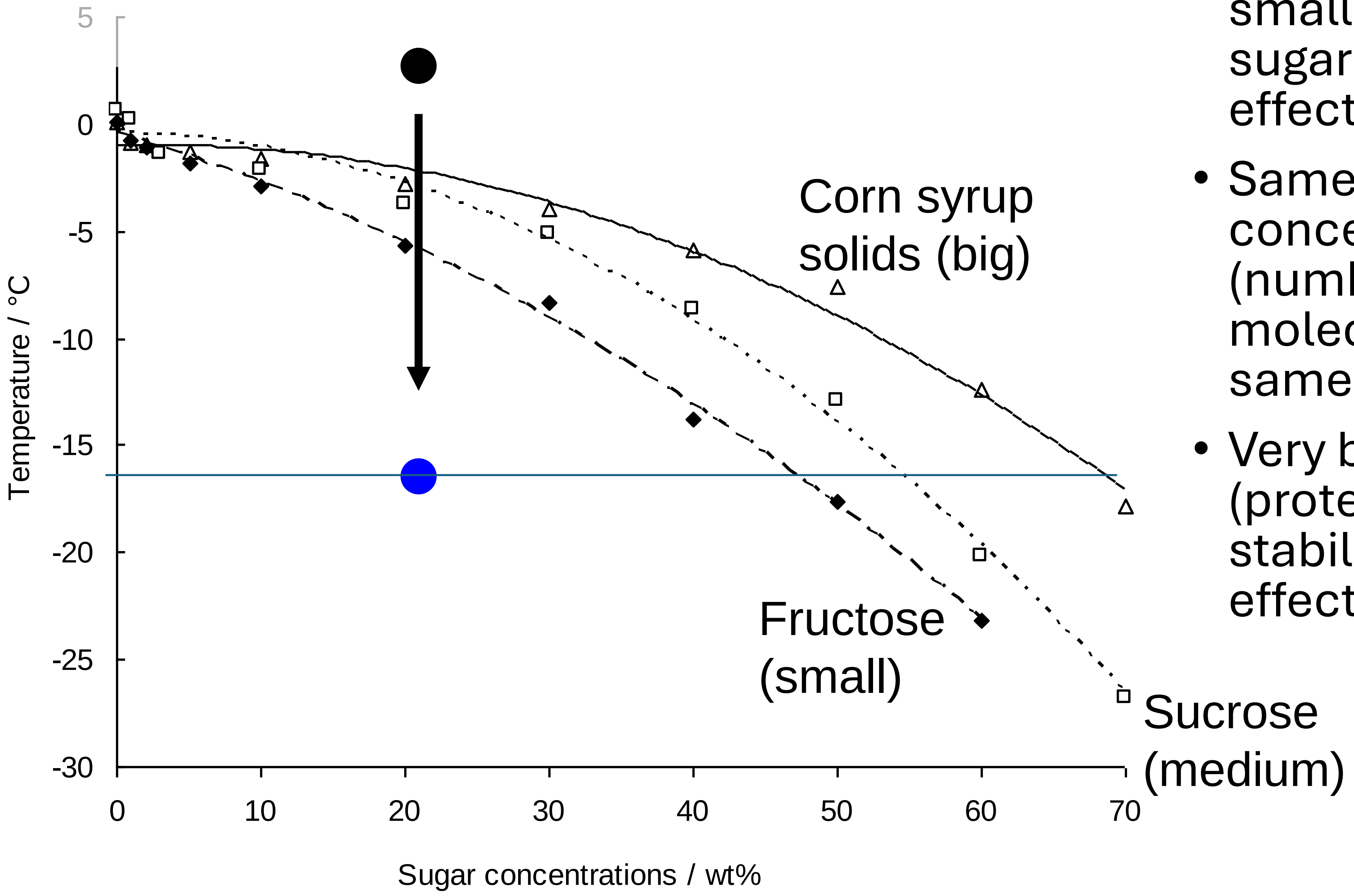
Solution

- Higher entropy -> even steeper slope

Freezing point decreases with solution concentration

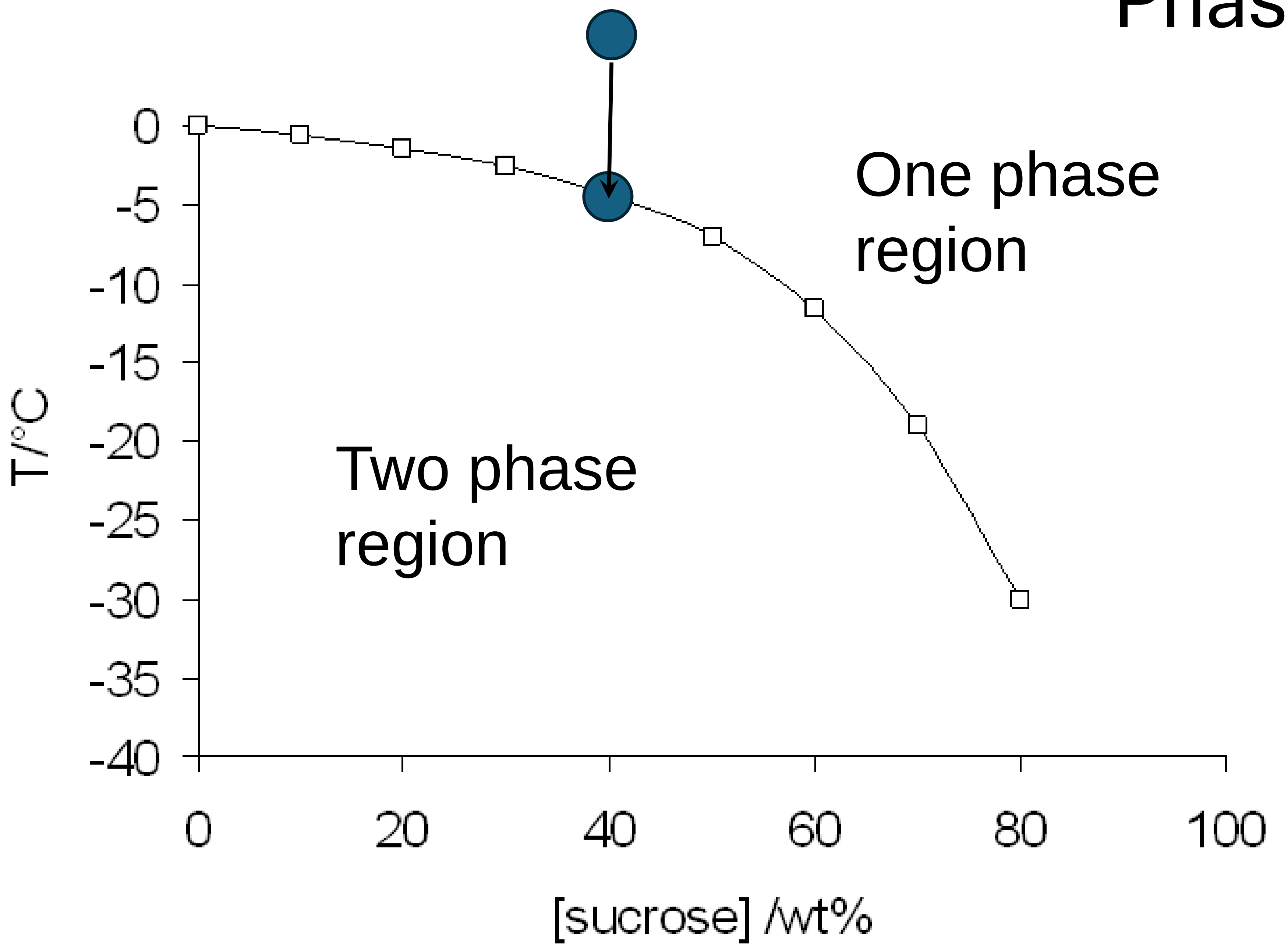


Smaller molecules do more

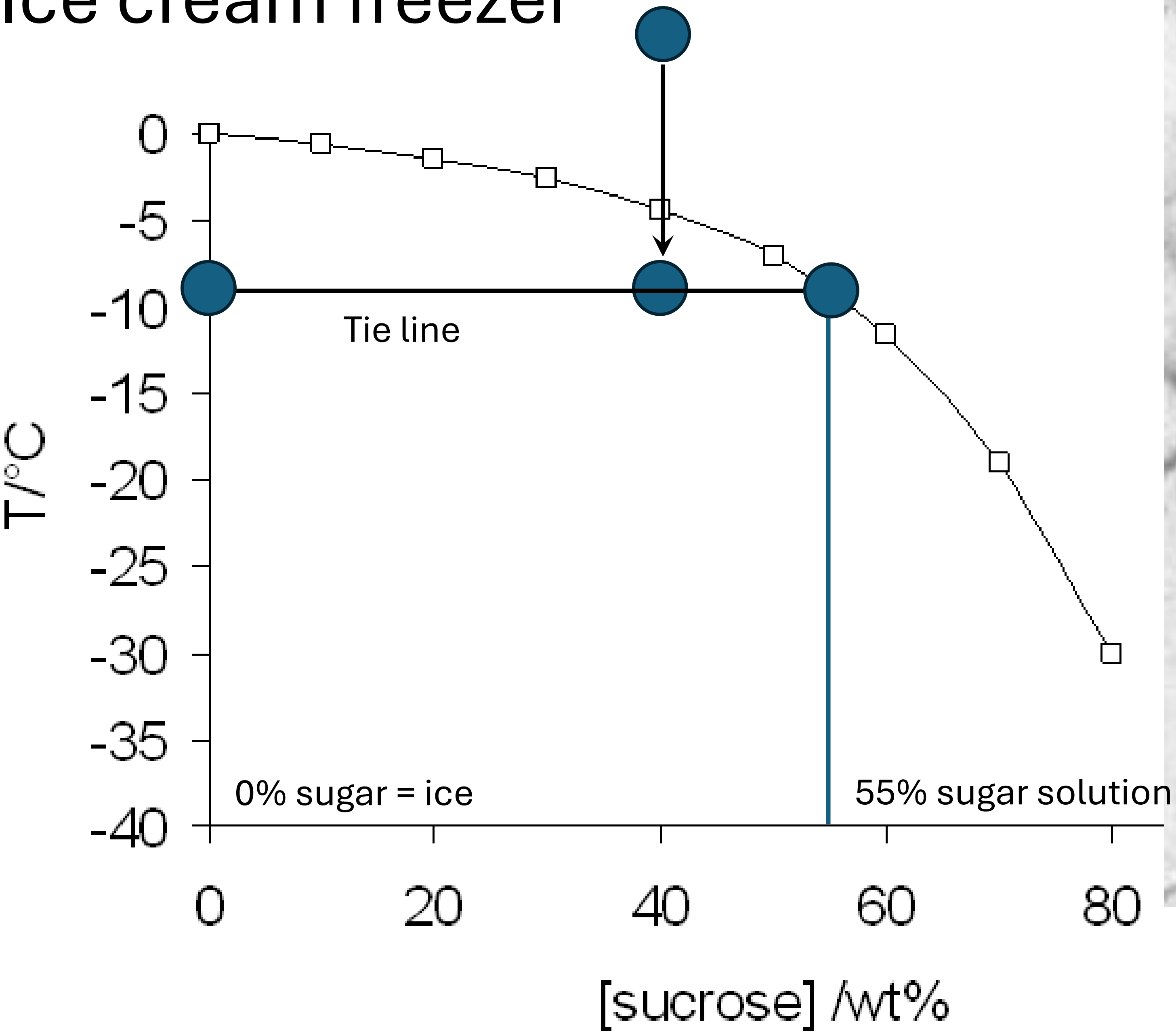


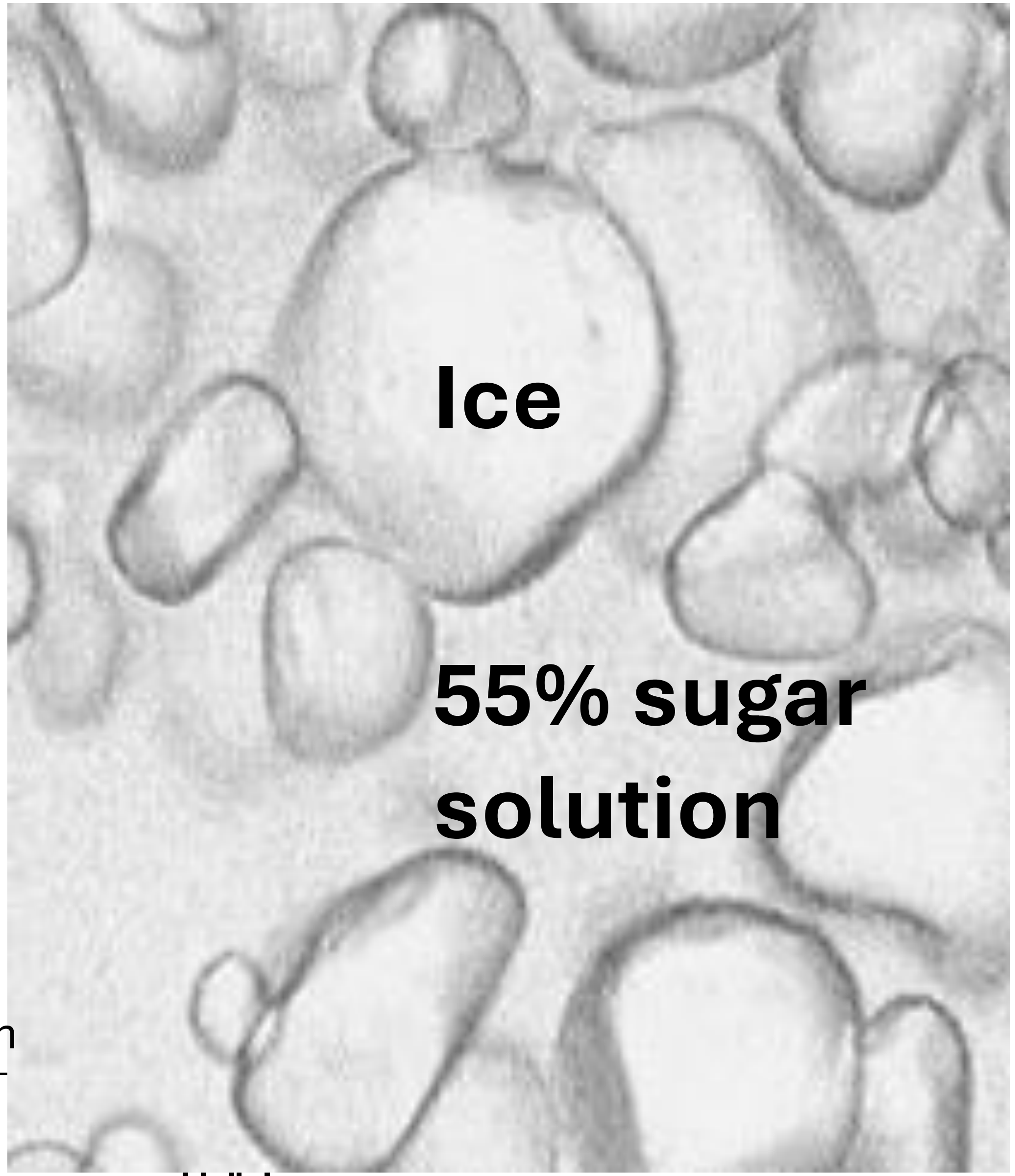
- Same mass concentration of a smaller molecule sugar has a bigger effect
- Same molar concentration (number of solute molecules) has the same effect
- Very big molecules (proteins and stabilizers) have no effect

Phase diagram

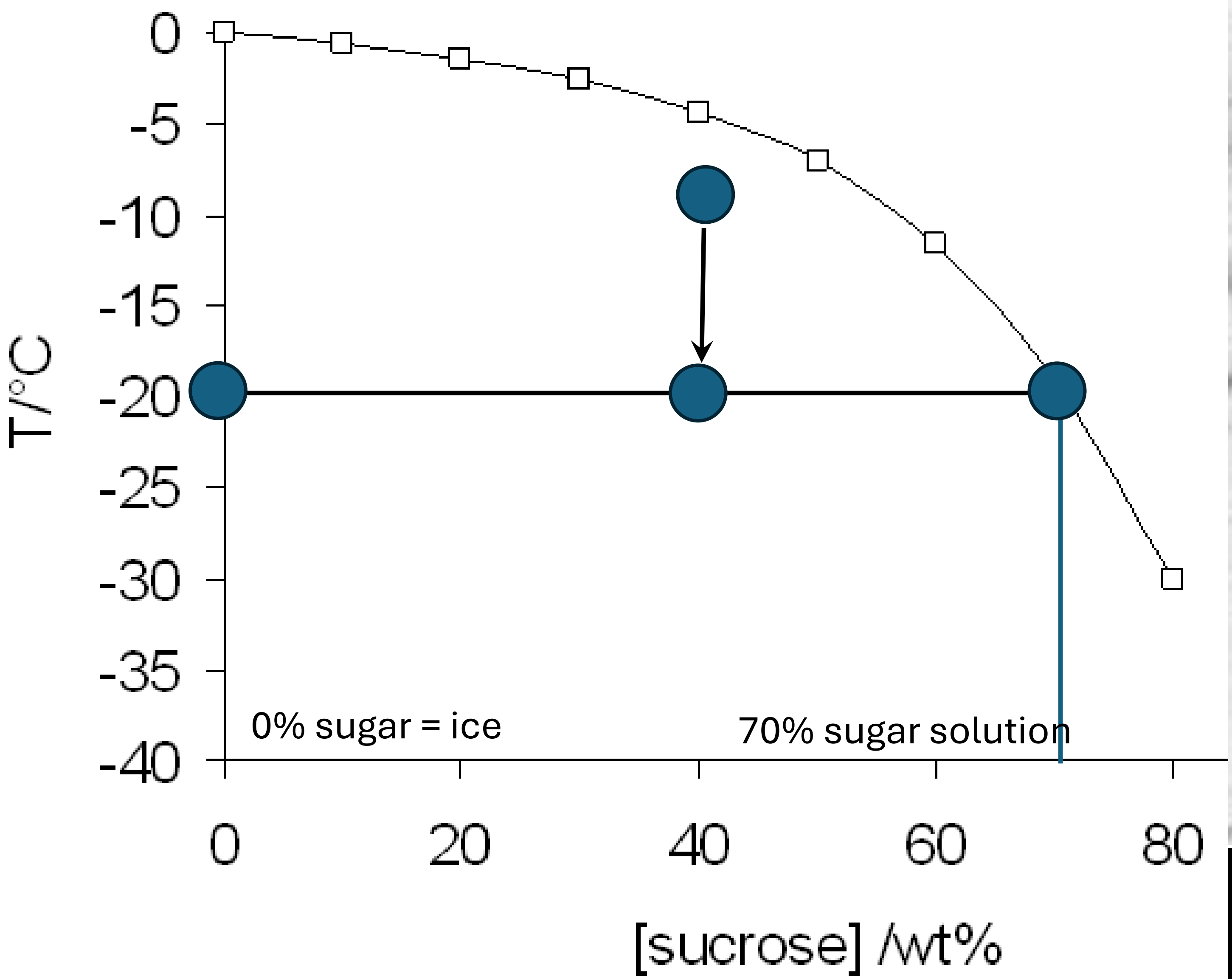


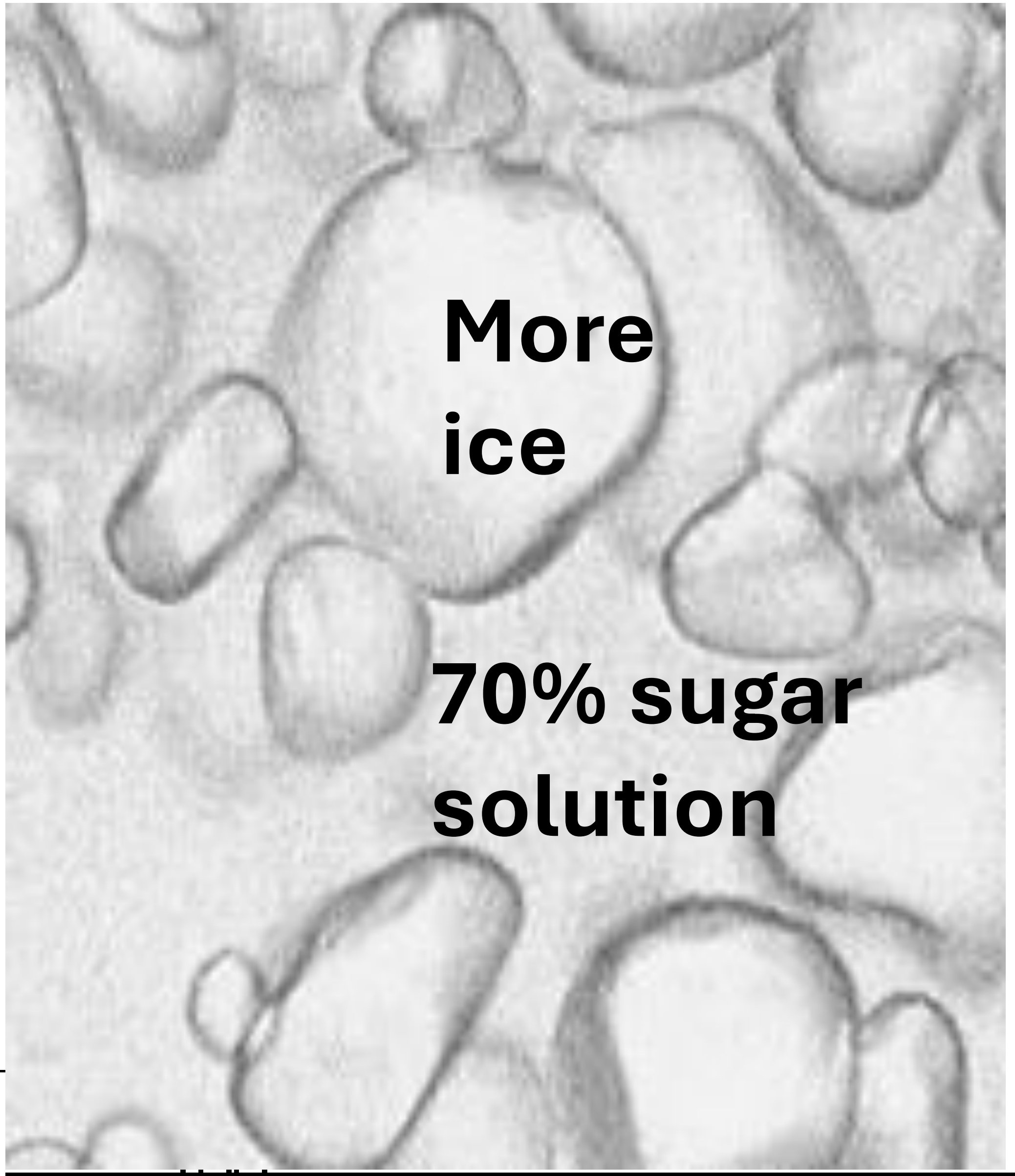
Ice cream freezer





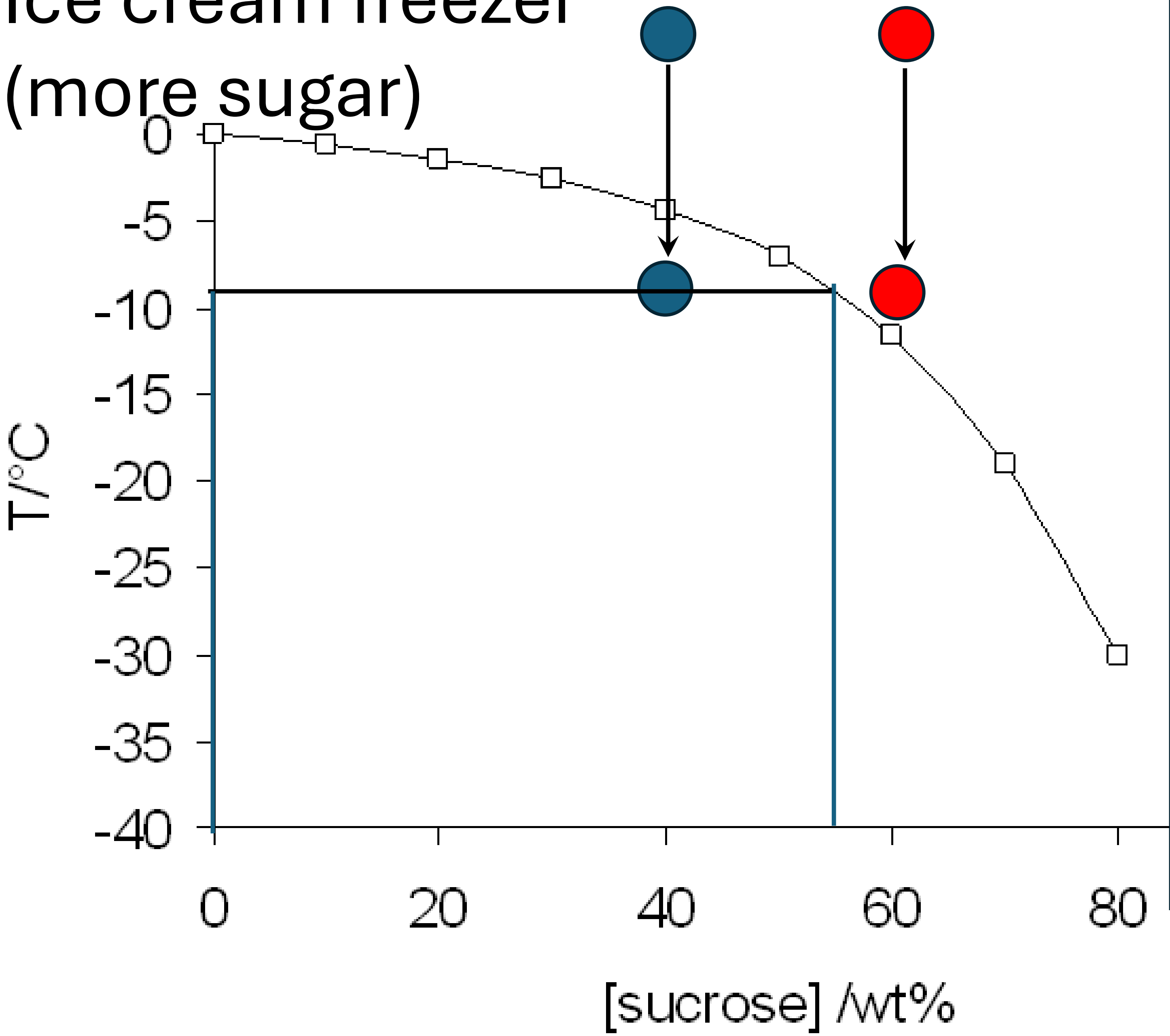
Hardening room





Ice cream has more ice at lower temperatures

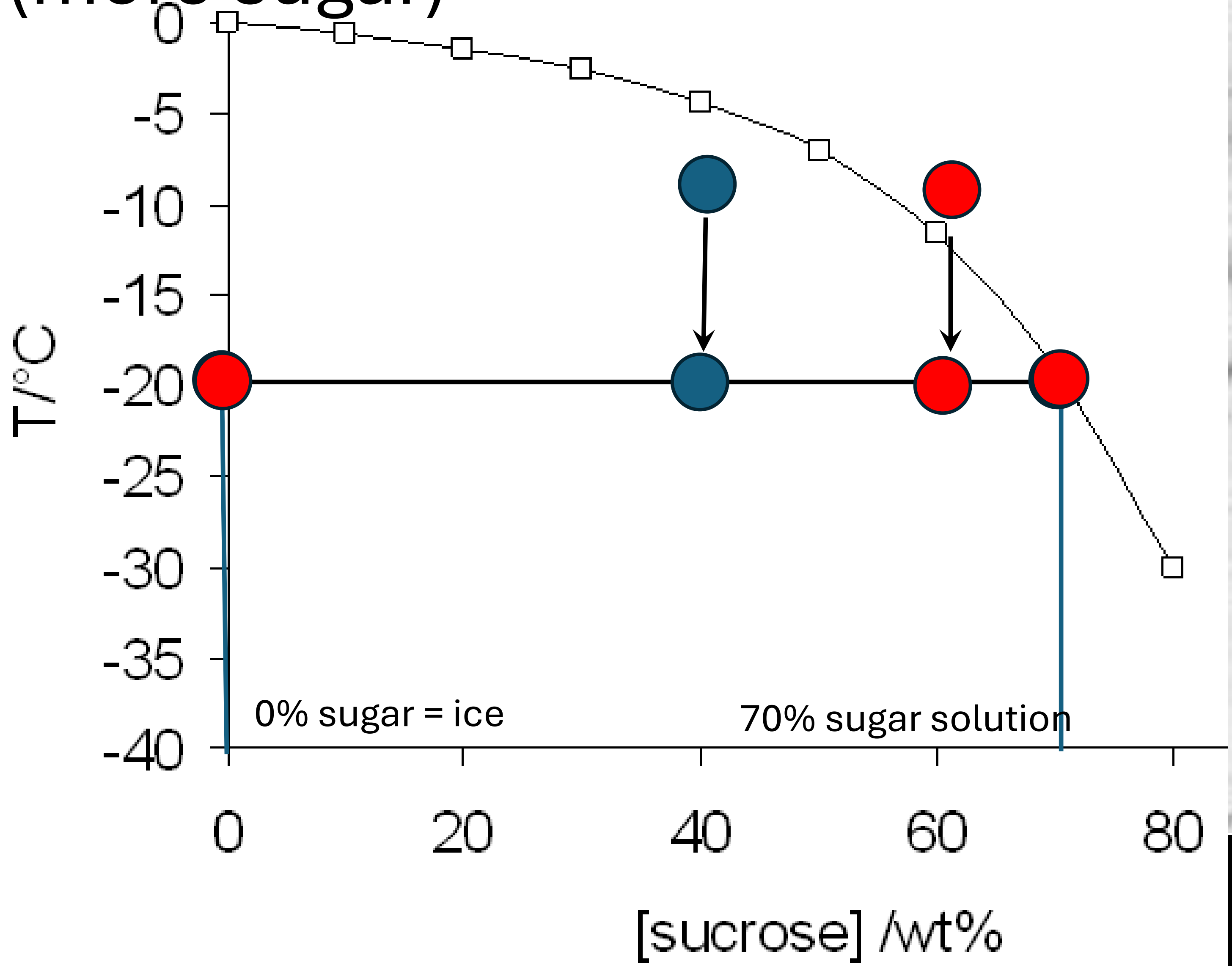
Ice cream freezer (more sugar)

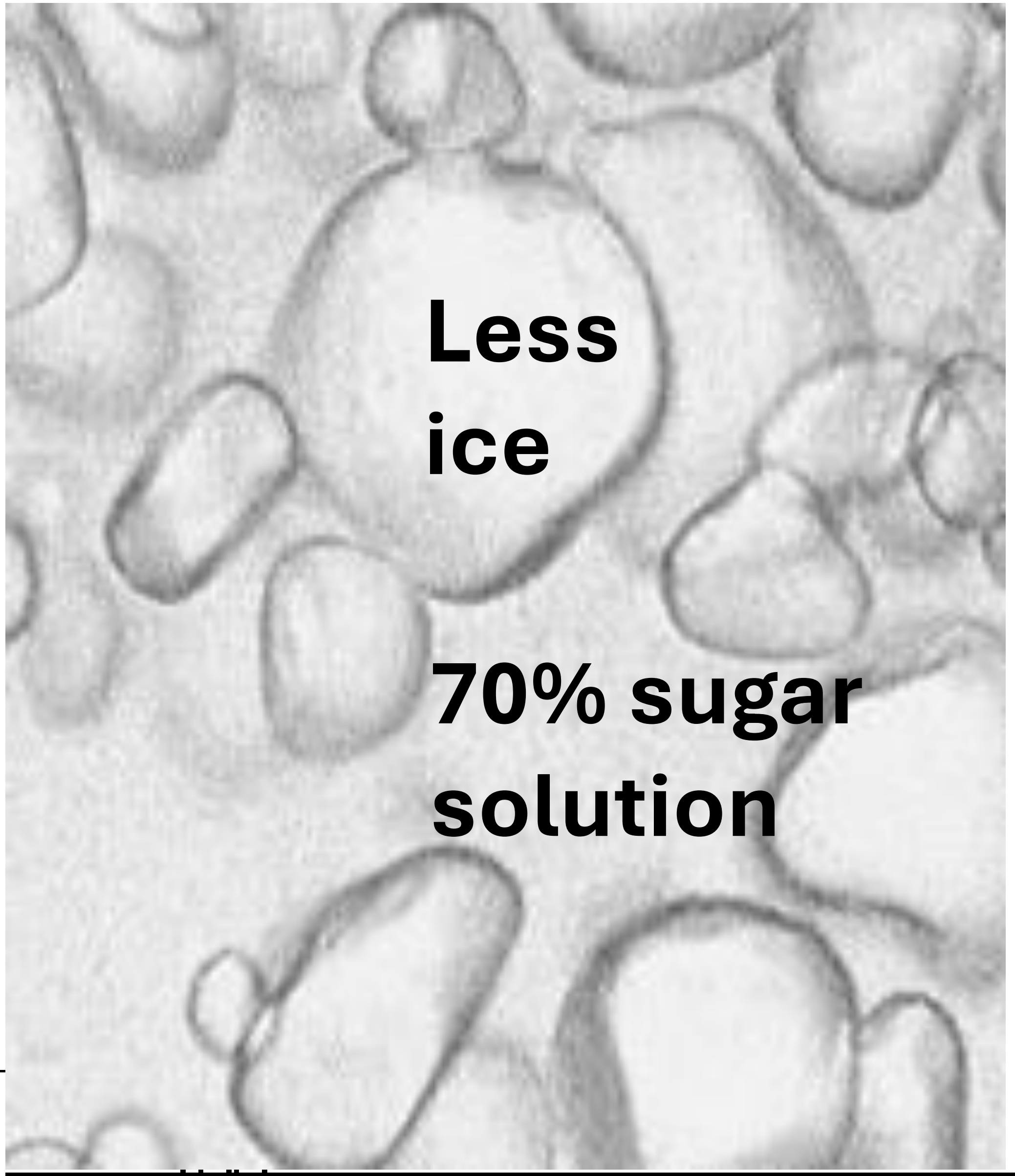


60% sugar solution (unfrozen)

Ice cream has less ice at higher sugar concentrations

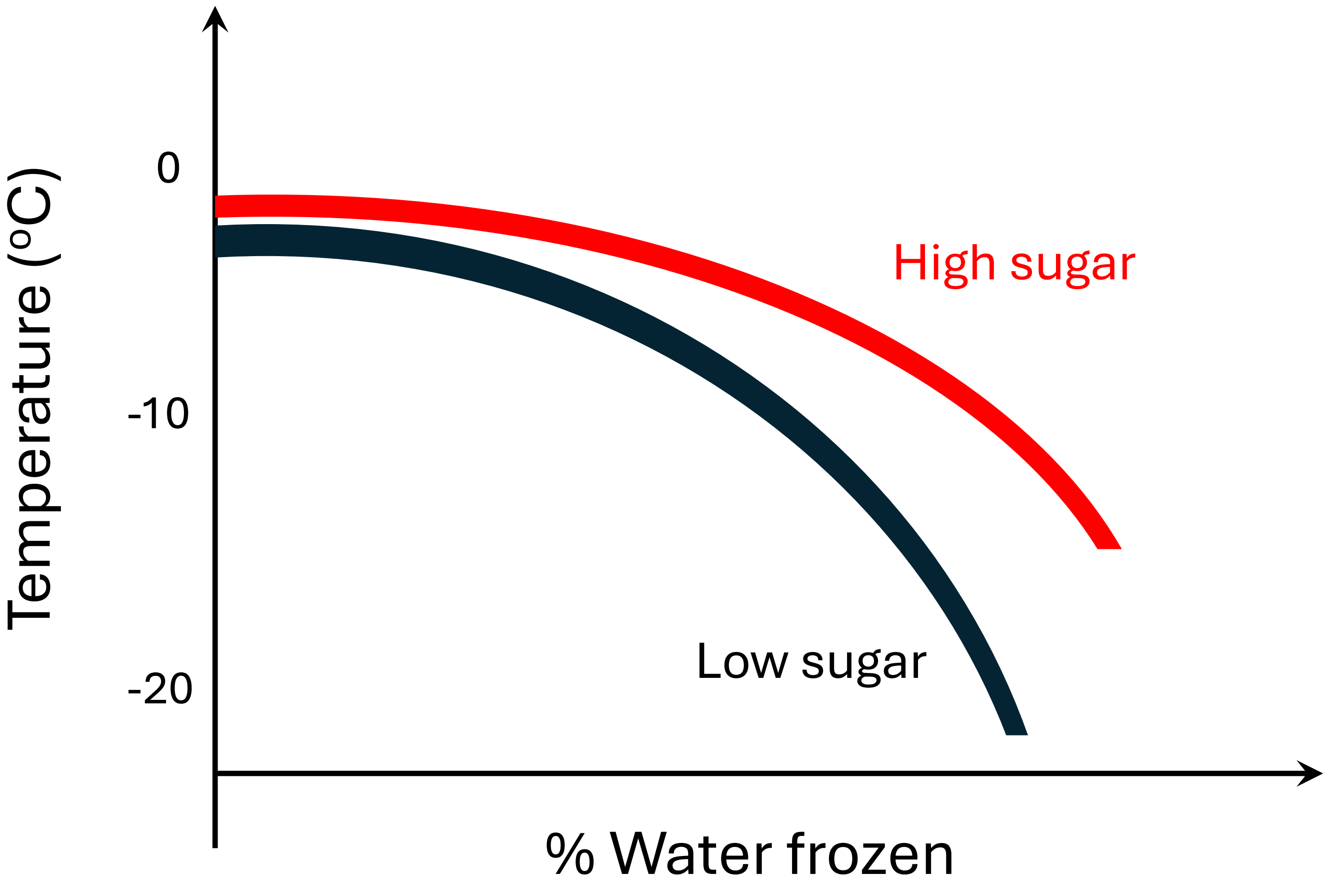
Hardening room (more sugar)





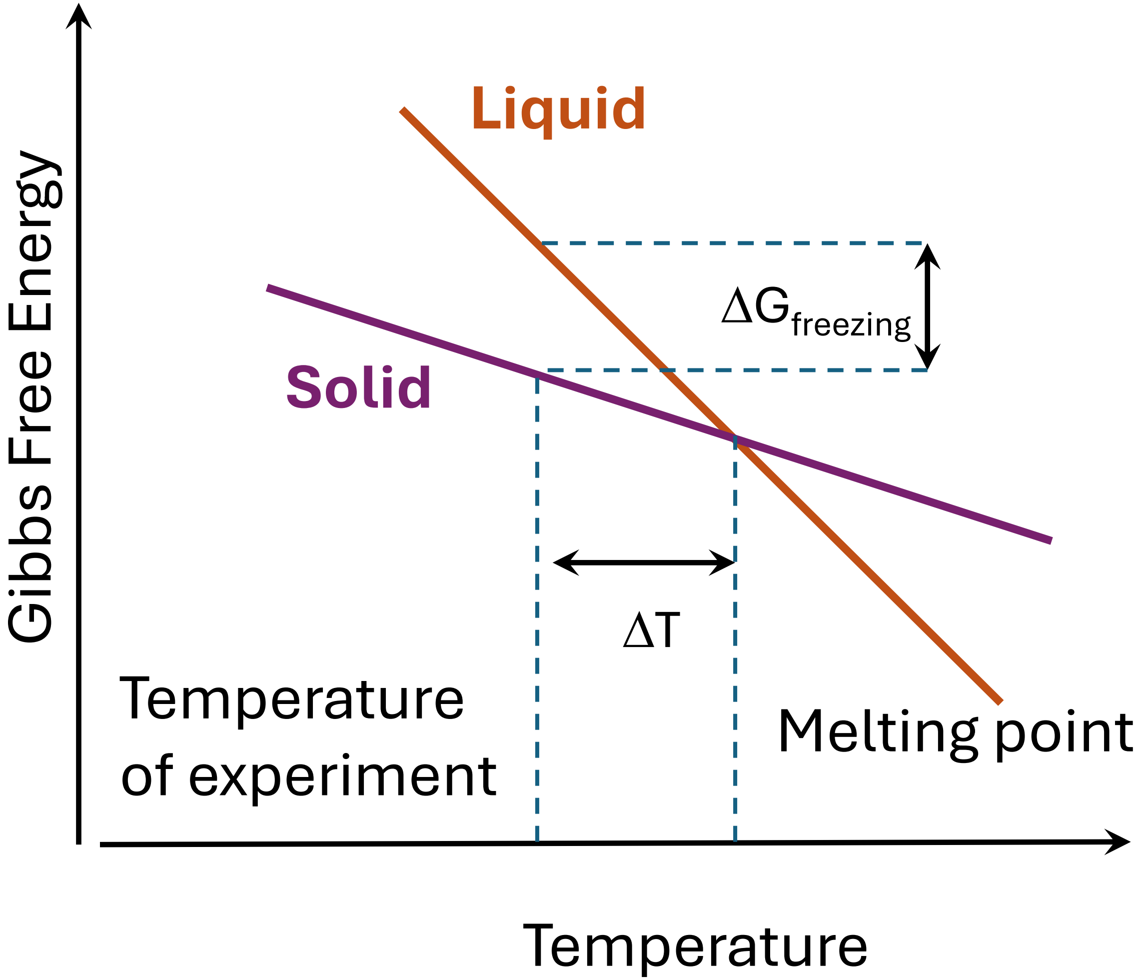
Ice cream has less ice at higher sugar concentrations

Ice cream freezing curves



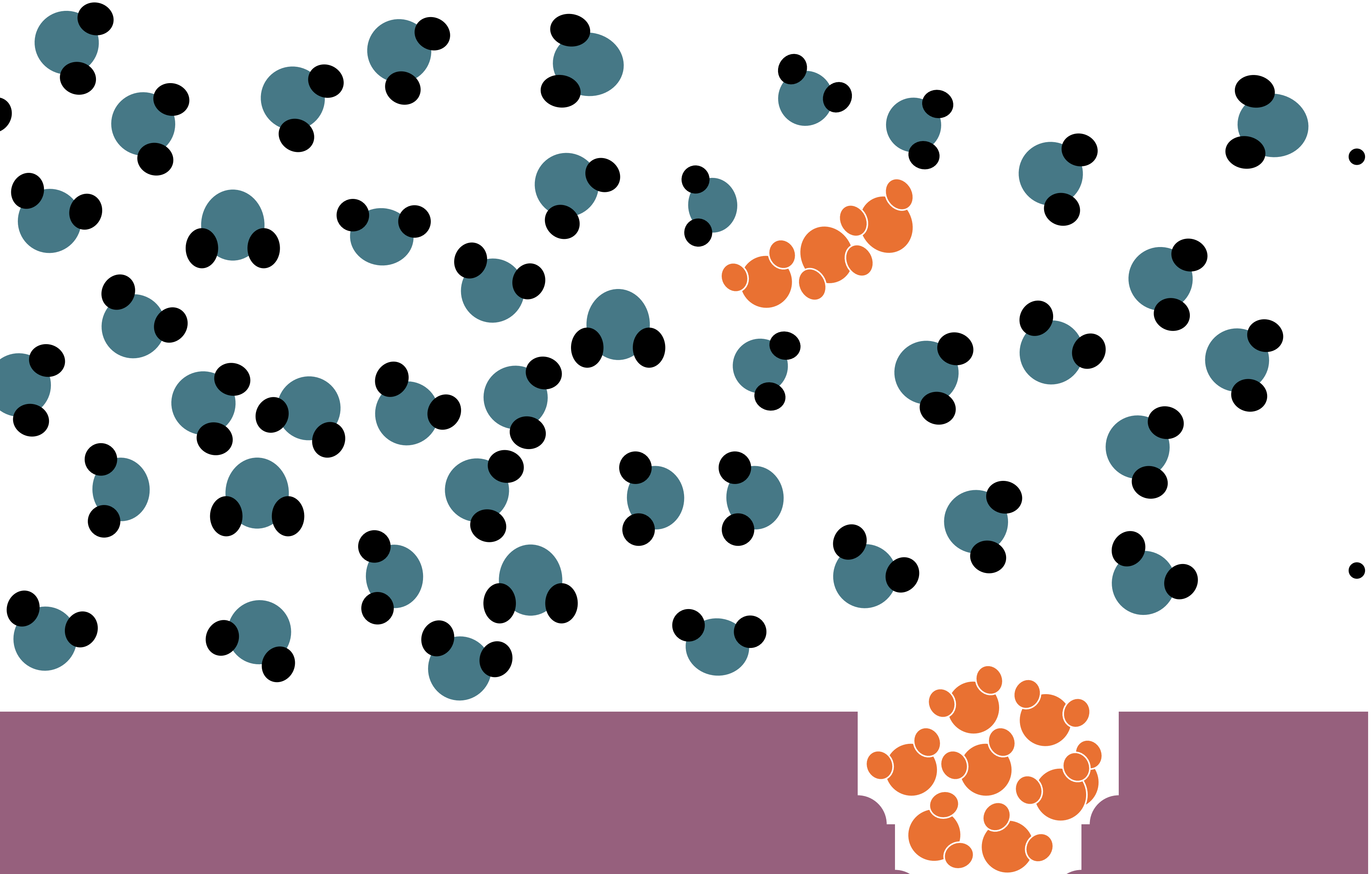
- Calculate freezing curves from composition
- Commercial software available
- Similar %frozen means similar texture. Important for scooping ice cream or pumping soft serve

Kinetics of Freezing



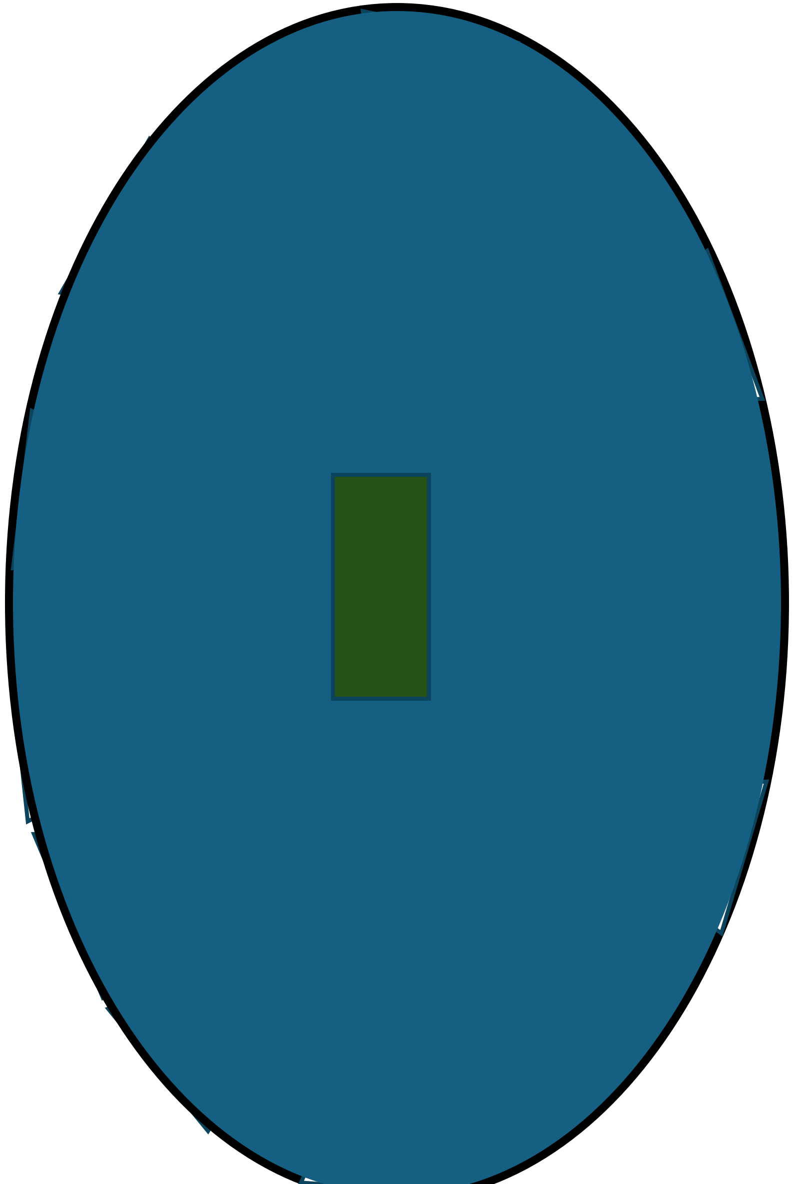
- Deeper the supercooling (undercooling, ΔT) the greater the thermodynamic driving force for freezing ($\Delta G_{freezing}$)
- Greater the driving force; faster the process
- But – water can stay supercooled for a long time

Crystal nucleation



- Small crystal nuclei (embryos) often simply break down again to liquid
- Until a nucleus lasts long enough to grow, no visible crystallization occurs
- Nucleation is easier at surfaces (heterogeneous)

Popsicle Microstructure



- Ice crystal nucleation occurs in the coldest place (deepest supercooling)
- Ice crystal nucleation occurs on the solid wall (heterogeneous nucleation)

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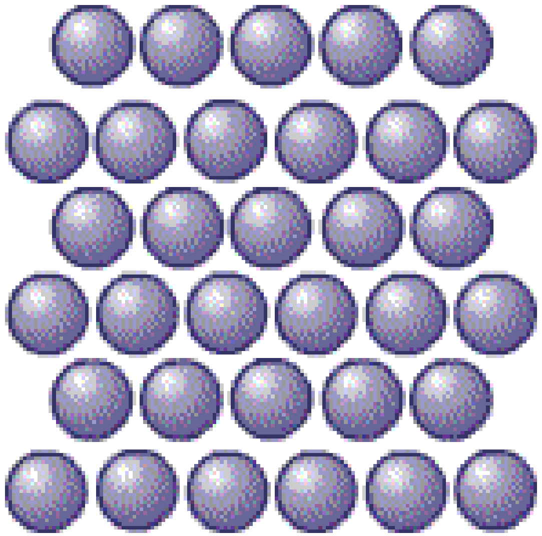
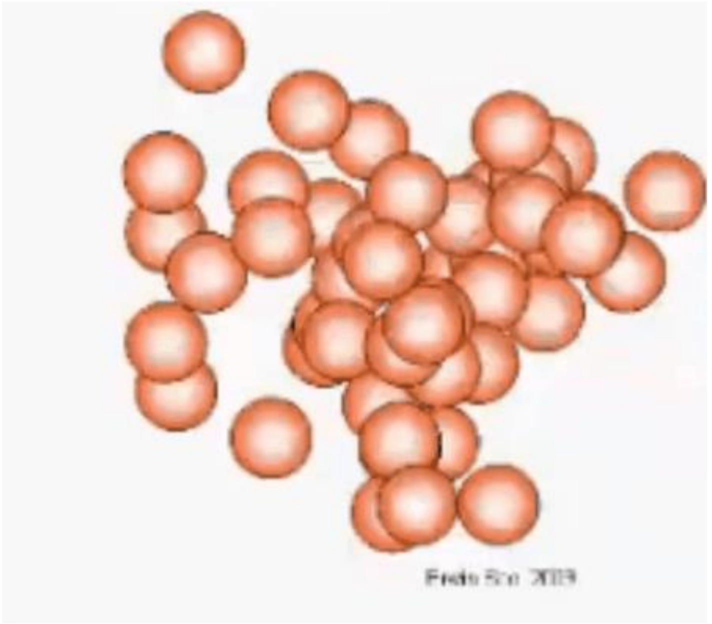


John Coupland
Penn State



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