# Chapter 10: Liquids and Solids

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CHM111

Lecture 10

# Key Concept

This chapter builds on one premise:

All condensed-phase behavior is a consequence of a pair potential $u(r)$ between molecules, composed of a steeply repulsive core plus a weakly attractive tail, averaged over thermal motion.

# Part I

# Intermolecular Forces

# Outline of Part I: Intermolecular Forces

Introduction

Intermolecular Forces

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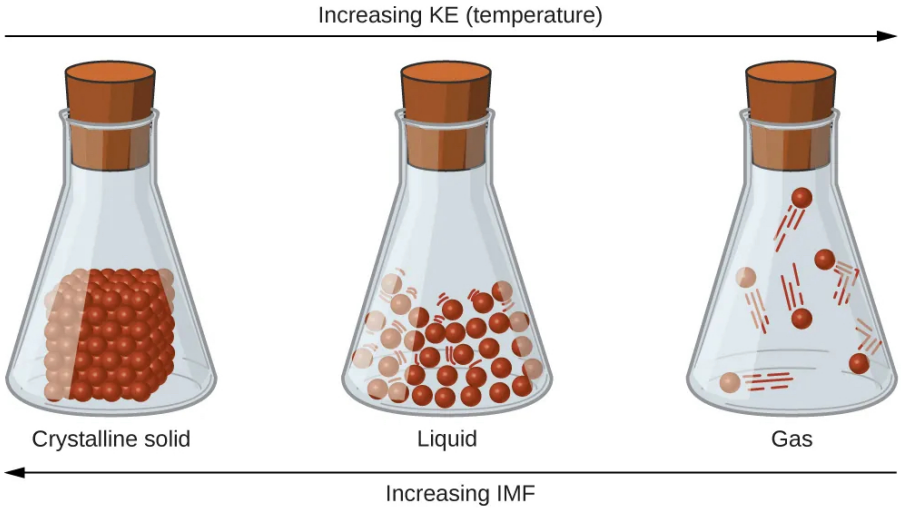
Introduction

Intermolecular Forces

# Chapter 10: Liquids and Solids



# Chapter 10: Liquids and Solids

Gas-phase molecules are far apart and nearly independent.

In **liquids** and **solids**, molecules are close together and strongly influenced by their neighbors.

Understanding intermolecular forces explains physical properties: boiling point, viscosity, surface tension, and the structure of solids.

# Chapter Overview

## Topics Covered in Chapter 10

1. **Intermolecular Forces** — dispersion, dipole-dipole, hydrogen bonding, ion-dipole
2. **Properties of Liquids** — surface tension, viscosity, capillary action
3. **Phase Transitions** — vaporization, condensation, melting, freezing, sublimation; vapor pressure; Clausius-Clapeyron equation
4. **Phase Diagrams** — triple point, critical point, water and $CO_2$ diagrams
5. **The Solid State** — crystalline vs. amorphous; ionic, metallic, covalent, molecular solids
6. **Lattice Structures** — unit cells, packing efficiency, density, X-ray diffraction

# *State* v. *Phase*

- **State** describes the *physical form* of matter (solid, liquid, or gas).
- **Phase** describes a *physically distinct*, uniform region of matter with the same composition and properties throughout.

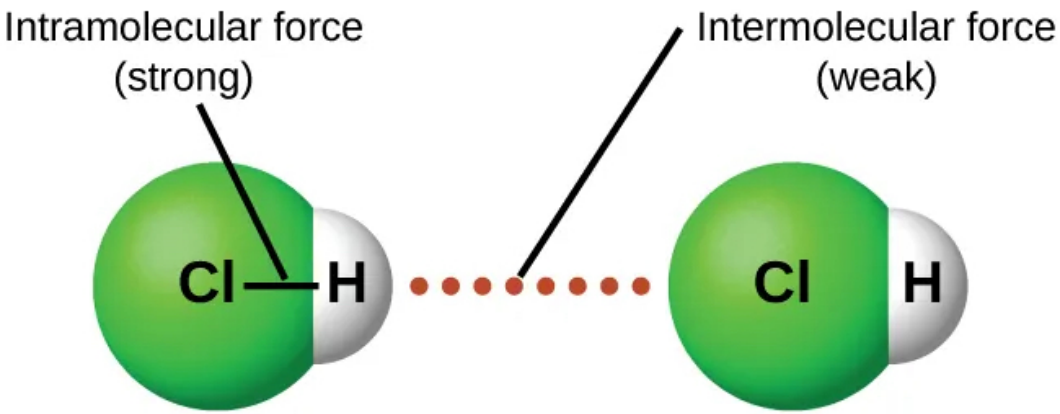
A system can contain multiple phases, even when all of the matter is in the same state. For example, oil and water are both liquids (one state), but because they are immiscible, they form two liquid phases: an oil phase and a water phase.

# Outline of Part I: Intermolecular Forces

Introduction

Intermolecular Forces

# Intermolecular vs. Intramolecular Forces



# Intermolecular vs. Intramolecular Forces

## Intramolecular Forces

**Within** a molecule — chemical bonds (covalent, ionic, metallic).

*Very strong*: breaking H–O bonds in water requires $\sim 925\ \frac{\text{kJ}}{\text{mol}}$.

## Intermolecular Forces (IMFs)

**Between** molecules — electrostatic attractions between partial or full charges.

*Much weaker*: breaking HCl IMFs requires only $\sim 17\ \frac{\text{kJ}}{\text{mol}}$.

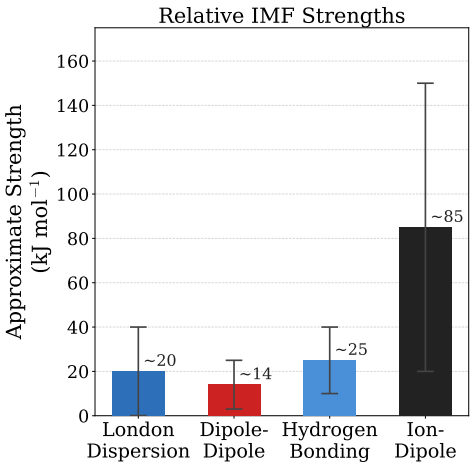
IMFs are about **5–25 times weaker** than covalent bonds, yet they control melting points, boiling points, viscosity, and surface tension.

Do not confuse: boiling **breaks IMFs**, not covalent bonds. Water molecules remain intact when water boils.

# The Four Types of IMFs

- **London Dispersion Forces** — present in *all* substances; caused by temporary dipoles
- **Dipole-Dipole Attractions** — between polar molecules with permanent dipoles
- **Hydrogen Bonding** — extra-strong dipole-dipole for H bonded to F, O, or N
- **Ion-Dipole Forces** — between an ion and a polar molecule

Strength generally:
London < Dipole-Dipole < H-Bond < Ion-Dipole



# One Interaction ⇒ Many Apparent Forces

- Question
  - Why do four IMF "types" appear if all originate from *Coulomb interaction*?
- Evidence
  - Ion–ion, ion–dipole, dipole–dipole, and London interactions involve separated charges.
  - Measured interaction energies decrease systematically with increasing charge separation.
- Reasoning
  - $\because$ Coulomb potential weakens with distance and charge cancellation, higher multipoles decay faster.
  - $\therefore$ Interaction strength follows distance scaling, not distinct physical mechanisms.
- Takeaway
  - One electrostatic mechanism explains all intermolecular interactions.

# How does the Electrostatic Atraction Vary for Different IMFs?

- Question
  - Why does electrostatic attraction change from $1/r$ to much steeper distance dependences?
- Evidence
  - An isolated ion creates a potential proportional to $1/r$.
  - Neutral molecules contain equal positive and negative charge that largely cancel far away.
- Reasoning
  - $\because$ Charge cancellation removes the leading $1/r$ term, only higher-order multipoles remain.
  - $\therefore$ Ion–ion $\sim r^{-1}$, ion–dipole $\sim r^{-2}$, dipole–dipole $\sim r^{-3}$, London $\sim r^{-6}$.
- Takeaway
  - Stronger charge cancellation causes faster distance decay.

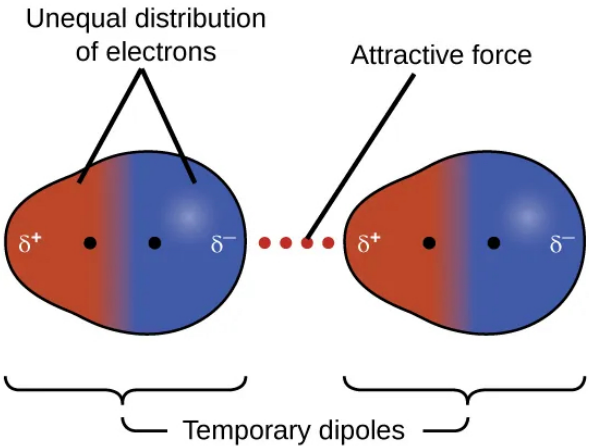
# Why Weak Forces Hold Liquids Together

- Question
  - Why do weak intermolecular forces stabilize condensed matter?
- Evidence
  - A liquid molecule interacts simultaneously with roughly 10–12 neighbors.
  - Typical IMF energies are tens of $\mathrm{kJ\,mol^{-1}}$ per interacting pair.
- Reasoning
  - $\because$ Many pair interactions contribute approximately additively around each molecule.
  - $\therefore$ Collective *pair potentials* rival or exceed one covalent bond.
- Takeaway
  - Many weak interactions create strong bulk cohesion.

# Why Boiling Breaks IMFs, But Not O – H Bonds

- Question
  - Why does boiling separate molecules without breaking covalent bonds?
- Evidence
  - At 100 °C, water vapor contains intact $H_2O$ molecules.
  - O–H bond potentials are much deeper and steeper than intermolecular potentials.
- Reasoning
  - $\because$ Thermal energy reaches shallow intermolecular wells before deep covalent wells.
  - $\therefore$ Heating overcomes IMFs while O–H bonds remain intact.
- Takeaway
  - *Potential-well depth* controls phase changes.

# London Dispersion Forces (LDFs)



# London Dispersion Forces (LDFs)

## Definition

**London dispersion forces** (LDFs, also called **van der Waals forces** or **induced-dipole forces**) arise from *temporary, instantaneous* dipoles created by random fluctuations in electron distribution.

## How They Arise

- At any instant, electrons may be unevenly distributed ⇒ **temporary dipole**.
- This temporary dipole induces a dipole in a neighboring atom/molecule.
- The two dipoles attract each other.
- These attractions are short-lived but occur constantly.

LDFs are present in **every** substance (atoms, nonpolar molecules, polar molecules, and ions). They are the *only* IMF in nonpolar substances.

# Why Do Two *Neutral* Atoms Attract?

- Question
  - Why do two neutral atoms attract? i.e. why is the ground-state energy for a two-atom system lower than that of two isolated atoms?
- Evidence
  - Noble gases liquefy despite spherical, neutral electron clouds.
  - Attraction remains even as temperature approaches absolute zero.
- Reasoning
  - Zero-point electronic fluctuations cannot vanish in quantum mechanics.
  - $\therefore$ correlated fluctuations lower the pair's ground-state energy through *electron correlation*.
- Takeaway
  - Quantum correlations create attraction without permanent dipoles.

# What Controls the Strength of This Attraction?

- Question
  - Which physical variables determine the interaction energy?
- Evidence
  - Larger atoms distort more easily, giving greater *polarizability* $\alpha$.
  - Electronic excitations introduce a characteristic energy $\hbar\omega$.
- Reasoning
  - Energy depends only on $\alpha$, $\hbar\omega$, and separation $r$.
  - $\therefore$ dimensional analysis gives $E \propto -C\alpha^2\hbar\omega/r^6$.
- Takeaway
  - Interaction strength follows measurable molecular properties.

# Why Does the Energy Fall as $r^{-6}$?

- Question
  - Why is the distance dependence $r^{-6}$ instead of $r^{-2}$ or $r^{-3}$?
- Evidence
  - The electric field produced by a point electric dipole decreases as $\sim r^{-3}$.
  - Interaction energy requires two mutually correlated dipole responses.
- Reasoning
  - One $r^{-3}$ factor describes each coupled dipole interaction.
  - $\therefore$ correlated interaction energy scales as $r^{-3} \times r^{-3} = r^{-6}$.
- Takeaway
  - Coupled dipole interactions produce rapid distance decay.

# Why Are London Dispersion Forces Chemically Short-Ranged?

- Question
  - How does the $r^{-6}$ law determine observable molecular behavior?
- Evidence
  - Doubling separation reduces attraction by 64 ($\because 2^6$).
  - Thermal motion disrupts LDFs once interaction energy approaches $k_B T$.
- Reasoning
  - Energy decreases much faster than ionic or permanent-dipole interactions.
  - $\therefore$ only near-contact, small separations yield dispersion attraction large enough to influence molecular behavior *despite* random thermal motion.
- Takeaway
  - Near-contact geometry governs dispersion-driven properties.

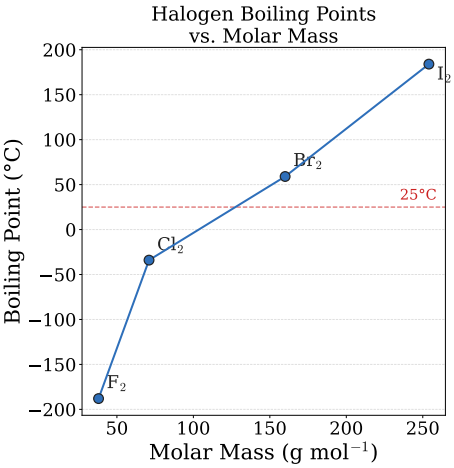
# Dispersion Forces: Size and Shape

## What Controls Their Strength?

- **Molar mass / number of electrons**: More electrons ⇒ more polarizable ⇒ stronger forces.
- **Molecular shape**: Elongated molecules have more surface contact area ⇒ stronger forces.

## Halogen Trend

| Substance | MW | State @ 25°C |
|---|---|---|
| $F_2$ | $38\ \frac{g}{mol}$ | gas |
| $Cl_2$ | $71\ \frac{g}{mol}$ | gas |
| $Br_2$ | $160\ \frac{g}{mol}$ | liquid |
| $I_2$ | $254\ \frac{g}{mol}$ | solid |

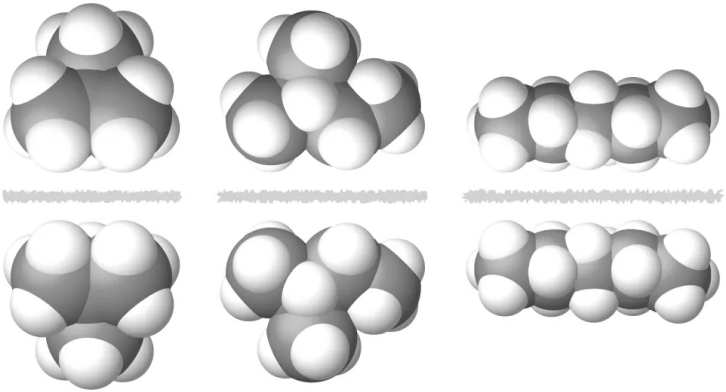


# Dispersion Forces: Molecular Shape Effect

Small contact area,
weakest attraction

Less surface area,
less attraction

Large contact area,
strong attraction



neopentane
boiling point: 9.5 °C

isopentane
boiling point: 27 °C

*n*-pentane
boiling point: 36 °C

# Dispersion Forces: Molecular Shape Effect

## Pentane Isomers

All three isomers have the same molecular formula ($C_5H_{12}$, MW $= 72\,\frac{g}{mol}$) but different boiling points:

| **Isomer** | **Shape** | **Boiling Point** |
|---|---|---|
| *n*-pentane | linear (elongated) | 36 °C |
| isopentane | branched | 27 °C |
| neopentane | compact (spherical) | 9.5 °C |

More elongated ⇒ greater surface contact area ⇒ stronger dispersion forces ⇒ **higher boiling point**.
Compact/spherical shape ⇒ less contact area ⇒ weaker forces ⇒ **lower boiling point**.

# Why Are Larger Electron Clouds More Polarizable?

- Question
  - Why does a larger atom develop a larger induced dipole?
- Evidence
  - Outer electrons occupy larger average distances from the nucleus.
  - Induced dipoles increase down many elemental groups.
- Reasoning
  - Weakly bound electrons shift farther in an applied electric field.
  - $\therefore$ larger electron clouds have greater *polarizability* $\alpha$.
- Takeaway
  - Electron-cloud size controls polarizability.

# How Does Polarizability Affect Dispersion?

- Question
  - Why do larger, more polarizable molecules attract more strongly?
- Evidence
  - London energy scales as $-C\alpha^2/r^6$.
  - Separation is unchanged when comparing equal-contact molecules.
- Reasoning
  - Increasing $\alpha$ increases the interaction numerator.
  - $\therefore$ more polarizable molecules experience stronger *dispersion* attraction.
- Takeaway
  - Polarizability sets interaction strength.

# Why Does Molecular Shape Matter?

- Question
  - Why does $n$-pentane boil higher than neopentane?
- Evidence
  - Both molecules contain the same atoms and electrons.
  - Elongated molecules place more atoms near neighboring molecules.
- Reasoning
  - $\because$ the $r^{-6}$ interaction is dominated by near-contact atom pairs.
  - $\therefore$ elongated shapes sum more strong pairwise attractions.
- Takeaway
  - Shape controls the number of strong contacts.

# Why Do Halogen Boiling Points Rise Nonlinearly?

- Question
  - Why is boiling point not proportional to molar mass?
- Evidence
  - Boiling points increase rapidly from $F_2$ to $I_2$.
  - Polarizability also increases strongly down the group.
- Reasoning
  - $\because$ dispersion depends on *polarizability*, not directly on mass.
  - $\therefore$ mass predicts boiling point only by correlating with larger electron clouds.
- Takeaway
  - Polarizability, not mass, determines dispersion.

# Check Your Understanding

Which substance has the **stronger** London dispersion forces?

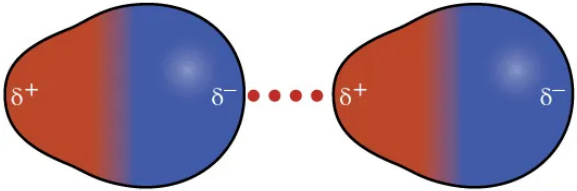
(a) $CH_4$ or $SiH_4$?

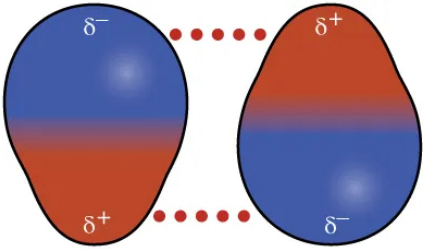
(b) *n*-pentane or neopentane?

(c) $Br_2$ or $Cl_2$?

Come to lecture to see the answer.

# Dipole-Dipole Attractions



# Dipole-Dipole Attractions

## Definition

**Dipole-dipole attractions** are electrostatic forces between the partially positive ($\delta^+$) end of one polar molecule and the partially negative ($\delta^-$) end of a neighboring polar molecule.

## Example: HCl

HCl is polar ($\mu \neq 0$); the $\delta^+$ H end of one HCl aligns with the $\delta^-$ Cl end of another.

HCl boils at $-85\,^\circ\mathrm{C}$; nonpolar Ar ($40\,\frac{\mathrm{g}}{\mathrm{mol}}$, similar MW) boils at $-186\,^\circ\mathrm{C}$.

The dipole-dipole attraction raises the boiling point significantly.

Dipole-dipole forces only operate when molecules are **aligned**.

In solids, molecules are well-aligned.
In liquids, alignment is partial and temporary.

# Why do Rotating Dipoles still Attract?

- Question
  - Why does freely rotating polarity produce net attraction instead of averaging to zero?
- Evidence
  - Polar liquids condense more readily than comparable nonpolar liquids.
  - Molecular rotation becomes slower as temperature decreases.
- Reasoning
  - $\because$ attractive orientations have lower potential energy, molecules spend slightly longer aligned than misaligned.
  - $\therefore$ thermal averaging leaves a net attraction that strengthens as temperature falls.
- Takeaway
  - Thermal motion weakens orientation-dependent attractions.

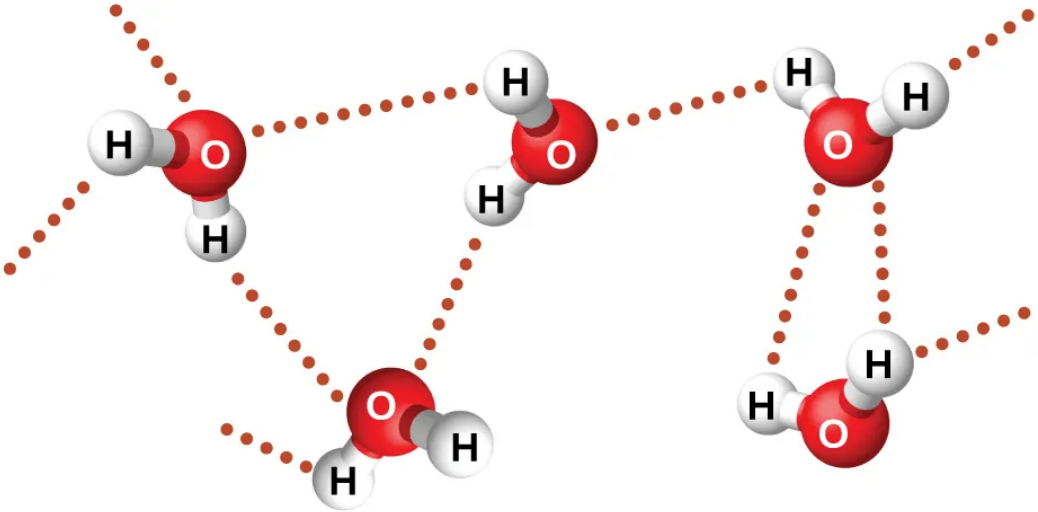
# Why Averaged Dipole Forces Resemble Dispersion

- Question
  - Why does the averaged attraction decay like dispersion rather than fixed dipoles?
- Evidence
  - A fixed dipole interaction depends strongly on molecular orientation.
  - Freely rotating molecules sample many orientations before separating.
- Reasoning
  - $\because$ favorable and unfavorable orientations nearly cancel, only the small energetic preference for alignment survives averaging.
  - $\therefore$ the remaining interaction decays much faster, matching the effective distance dependence of dispersion.
- Takeaway
  - Thermal averaging suppresses long-range dipole alignment.

# Why HCl Boils much Higher than Ar

- Question
  - Why is HCl's boiling point far above Ar despite similar mass?
- Evidence
  - HCl is polar whereas Ar has no permanent dipole.
  - Both substances possess electron clouds that produce dispersion forces.
- Reasoning
  - $\because$ HCl combines dispersion, induced-dipole, and thermally averaged dipole attractions, the measured cohesion reflects all mechanisms simultaneously.
  - $\therefore$ no experiment uniquely partitions their individual contributions.
- Takeaway
  - Intermolecular forces act together, not independently.

# Hydrogen Bonding



# Hydrogen Bonding

## Definition

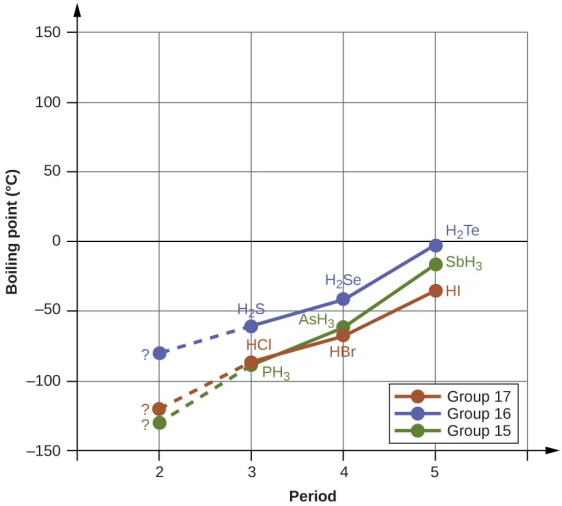
**Hydrogen bonding** is an especially strong dipole-dipole interaction that occurs when hydrogen is bonded to a highly electronegative atom — **F**, **O**, or **N** ("FON").

## Why Is It So Strong?

- H is tiny; when bonded to F, O, or N, the shared electrons are pulled far away.
- H is nearly a "bare proton" — its $\delta^+$ charge is concentrated in a very small volume.
- The result is a very strong partial charge that attracts the lone pairs of F, O, or N on neighboring molecules.

H-bonds are ~5–10% as strong as covalent bonds, but **much stronger** than ordinary dipole-dipole forces. They occur between **different** molecules (intermolecular) or within large molecules (intramolecular, e.g. DNA).

# Hydrogen Bonding: The Anomaly of $H_2O$, HF, $NH_3$



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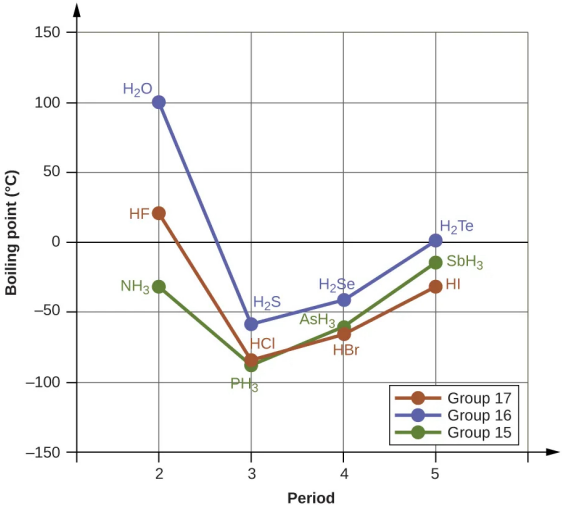
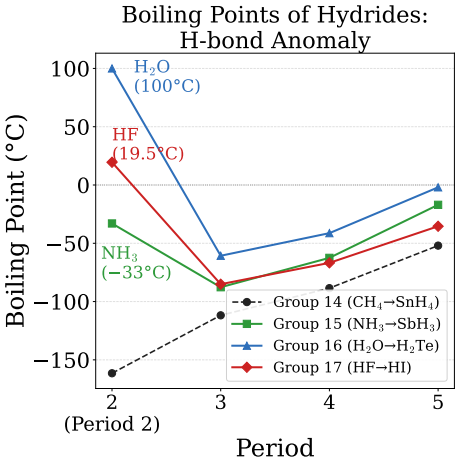


# Hydrogen Bonding: The Anomaly of $H_2O$, HF, $NH_3$

For group 14 hydrides ($CH_4$, $SiH_4$, $GeH_4$, $SnH_4$), boiling points increase smoothly with molar mass — as expected for dispersion forces only.

But for groups 15, 16, and 17, the lightest hydrides (**$NH_3$**, **$H_2O$**, **HF**) have **anomalously high** boiling points because of hydrogen bonding.

Without H-bonding, water would boil near $-70\,°C$.



# Why Hydrogen Forms Exceptional Intermolecular Bonds

- Question
  - Why can hydrogen create much stronger attractions than ordinary permanent dipoles?
- Evidence
  - H bonded to F, O, or N leaves hydrogen nearly electron-free.
  - Hydrogen has no inner electron shell shielding its nucleus.
- Reasoning
  - $\because$ an acceptor lone pair approaches the exposed proton unusually closely, electrostatic attraction and orbital overlap both increase.
  - $\therefore$ *hydrogen bonding* exceeds ordinary dipole attraction.
- Takeaway
  - Close orbital approach creates exceptionally strong intermolecular attraction.

# Why F, O, And N Dominate Hydrogen Bonding

- Question
  - Why does chlorine form much weaker hydrogen bonds than nitrogen?
- Evidence
  - Chlorine is larger than nitrogen despite comparable lone-pair availability.
  - F–H$\cdots$F bonds are stronger than O–H$\cdots$O bonds.
- Reasoning
  - $\because$ larger atoms keep lone pairs farther from hydrogen, orbital overlap and charge transfer decrease.
  - $\therefore$ small, highly electronegative atoms produce the strongest hydrogen bonds.
- Takeaway
  - Distance controls hydrogen-bond strength through orbital overlap.

# Why Water Defies the Hydride Boiling Trend

- Question
  - Why does water boil far above the smooth hydride trend?
- Evidence
  - Group-14 hydrides show a smooth dispersion-controlled boiling-point trend.
  - Extrapolation predicts $H_2O$ near $-70°C$ without hydrogen bonding.
- Reasoning
  - $\because$ dispersion changes smoothly with molecular size, the extrapolated value estimates non-hydrogen-bonded behavior.
  - $\therefore$ most of water's boiling-point elevation arises from its hydrogen-bond network.
- Takeaway
  - Deviations reveal additional intermolecular mechanisms.

# How Strong Is A Hydrogen Bond?

- Question
  - Why are hydrogen bonds substantial yet weaker than covalent bonds?
- Evidence
  - Hydrogen bonding shifts vibrational frequencies and lengthens donor bonds.
  - Breaking hydrogen-bonded networks requires measurable enthalpy.
- Reasoning
  - $\because$ partial electron sharing alters bond energies without forming full covalent occupancy.
  - $\therefore$ hydrogen bonds reach roughly 5–10% of covalent bond strength.
- Takeaway
  - Partial covalency gives hydrogen bonds unusual strength.

# Real-World Examples of IMFs

## Gecko Adhesion — Dispersion Forces

Gecko feet have millions of tiny hairs (setae) that branch into nanoscale tips.

The enormous surface area between tips and the wall creates enough **London dispersion forces** to support many times the gecko's weight.

## DNA — Hydrogen Bonding

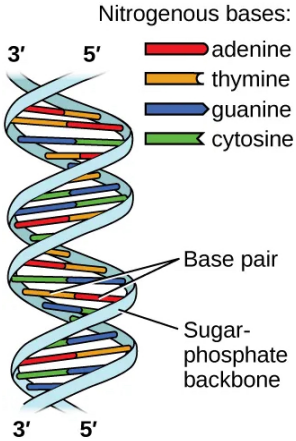
Complementary base pairs are held together by **hydrogen bonds**:

- Adenine-Thymine: **2** H-bonds
- Cytosine-Guanine: **3** H-bonds

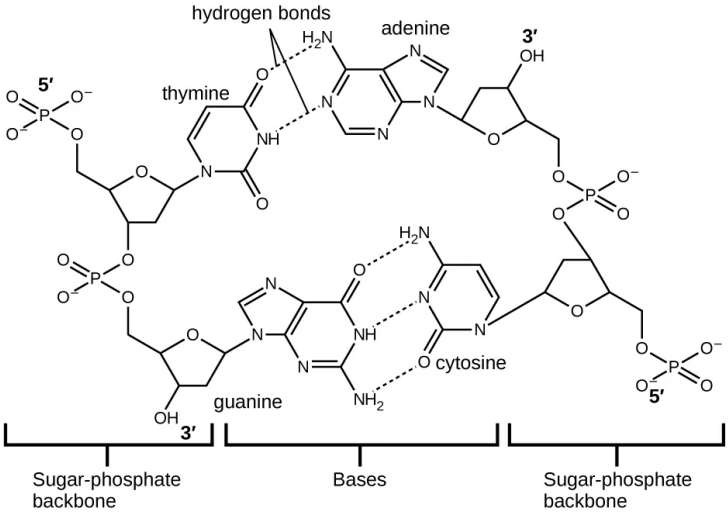
These bonds are weak enough that DNA can "unzip" for replication, yet strong enough to maintain the double helix.

IMFs may be weak individually, but they are enormously powerful **collectively**.

# DNA — Hydrogen Bonding



# DNA — Hydrogen Bonding



# Ion-Dipole Forces

## Definition

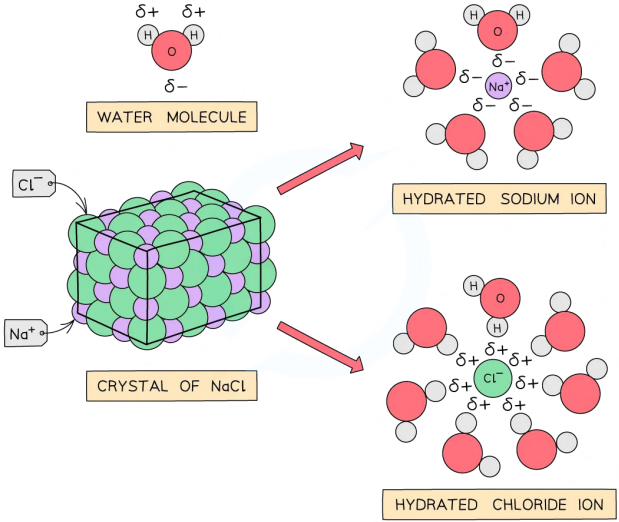
**Ion-dipole forces** are attractions between an **ion** (cation or anion) and the partially charged end of a **polar molecule**.

## Example: NaCl Dissolving in Water

- $Na^+$ ions attract the $\delta^-$ oxygen of $H_2O$ (water's O faces the cation).
- $Cl^-$ ions attract the $\delta^+$ hydrogen atoms of $H_2O$.
- Each ion is surrounded by a **hydration shell** of water molecules.
- Ion-dipole forces are strong enough to pull ions out of the crystal lattice.

Ion-dipole forces are the **strongest** of the four IMF types. They are responsible for the solubility of ionic compounds in polar solvents like water.

# Ion-Dipole Forces Cause NaCl to Dissolve in Water



# Why Does Ion–Dipole Interaction Reach Farther?

- Question
  - Why does an ion attract a polar molecule much farther than dispersion?
- Evidence
  - Water molecules orient around isolated ions several hydration shells away.
  - Dispersion attractions become negligible over similar distances.
- Reasoning
  - $\because$ An ion creates a persistent electric field that weakens gradually with distance and acts on opposite dipole charges.
  - $\therefore$ Dipole interaction energy decreases as $r^{-2}$, remaining significant after dispersion ($r^{-6}$) fades.
- Takeaway
  - *Field range* controls interaction distance.

# Why Does an Ion Consistently Orient Dipoles?

- Question
  - Why does thermal motion not average ion–dipole attraction to zero?
- Evidence
  - Water molecules preferentially point oxygen toward cations.
  - Neighboring permanent dipoles frequently lose preferred alignment.
- Reasoning
  - $\because$ An ion's isotropic electric field always exerts torque toward the same lowest-energy orientation despite molecular rotation.
  - $\therefore$ Thermal motion weakens alignment but cannot eliminate the net attractive orientation.
- Takeaway
  - Persistent fields overcome random molecular rotation.

# Why Do Small Highly Charged Ions Hydrate More Strongly?

- Question
  - Why are $Li^+$ and $Mg^{2+}$ hydrated *much more strongly* than $Cs^+$?
- Evidence
  - Small or multiply charged ions have much more negative hydration enthalpies.
  - Large singly charged ions release substantially less hydration energy.
- Reasoning
  - $\because$ Smaller or more highly charged ions create stronger electric fields where surrounding water molecules reside.
  - $\therefore$ Stronger ion–dipole attraction lowers potential energy, producing more exothermic hydration.
- Takeaway
  - *Field strength* predicts hydration energy.

# Check Your Understanding

Identify the **dominant** IMF(s) in each substance:

(a) $I_2$ (nonpolar, solid at room temp)

(b) HCl (polar)

(c) $CH_3OH$ (methanol, has O–H bond)

(d) NaBr dissolved in water

Come to lecture to see the answer.

# Part II

# Properties of Liquids

# Outline of Part II: Properties of Liquids

Properties of Liquids

# Outline of Part II: Properties of Liquids

Properties of Liquids

# Surface Tension $\gamma$

## Definition

**Surface tension** $\gamma$ (gamma) is the energy required to increase the surface area of a liquid (units: $\frac{\text{J}}{\text{m}^2}$ or $\frac{\text{N}}{\text{m}}$).

## Why Does It Occur?

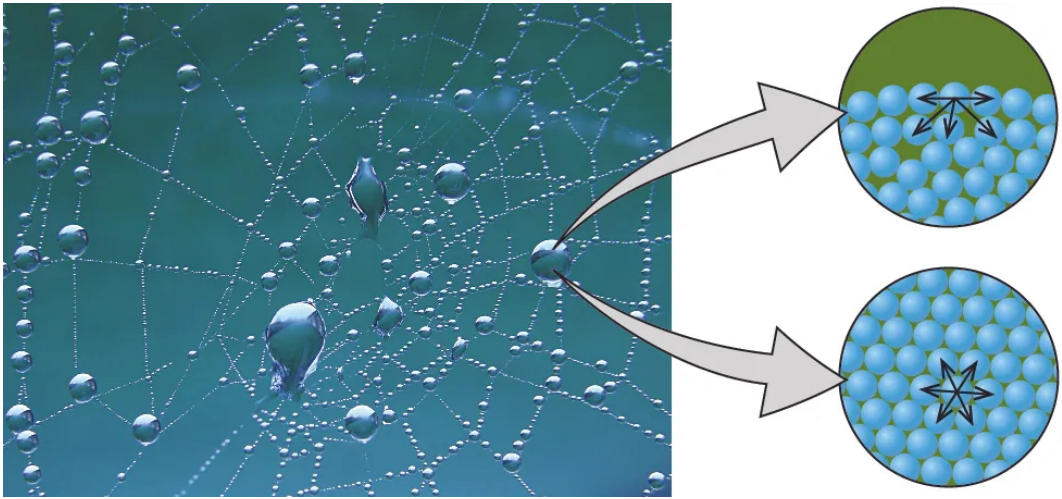
Molecules *at* the surface are only attracted by molecules *below* and *beside* them — the net force pulls them inward.

Molecules in the *interior* are attracted from all directions.

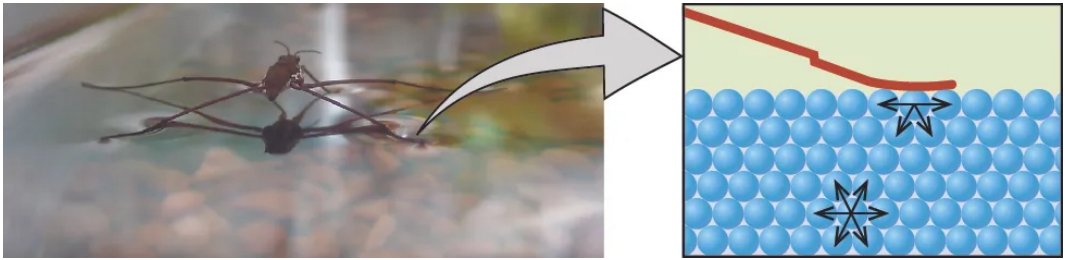
Liquids minimize their surface area $\Rightarrow$ water drops are spherical.

Stronger IMFs $\Rightarrow$ higher surface tension.
Mercury ($458\ \frac{\text{mN}}{\text{m}}$) $\gg$ water ($72\ \frac{\text{mN}}{\text{m}}$) $>$ ethanol ($22\ \frac{\text{mN}}{\text{m}}$).

# Surface Tension: Energy Needed to Stretch a Surface



# Surface Tension: Energy Needed to Stretch a Surface



# Where Does Surface Tension Come From?

- Question
  - Why does creating a liquid surface require energy?
- Evidence
  - Bulk molecules have about $z$ favorable nearest-neighbor contacts.
  - Surface molecules lose roughly half those attractive contacts.
- Reasoning
  - $\because$ Missing neighbors remove stabilizing intermolecular attractions, raising molecular free energy at the interface.
  - $\therefore$ Each surface molecule stores excess energy that becomes excess free energy per unit area, $\gamma$.
- Takeaway
  - *Missing intermolecular contacts* store interfacial free energy.

# Estimating the Magnitude of Surface Tension

- Question
  - Can molecular contact loss predict measured surface tensions?
- Evidence
  - Surface excess energy is about $z\varepsilon/2$ per molecule.
  - Molecular cross-sectional areas are typically a few $\text{Å}^2$.
- Reasoning
  - $\because$ Surface tension equals excess free energy divided by occupied interfacial area.
  - $\therefore$ Molecular estimates predict $\gamma \sim 10\text{–}500\,\text{mN}\,\text{m}^{-1}$, matching real liquids.
- Takeaway
  - Molecular energetics predict macroscopic surface tension.

# Why Do Liquids Minimize Surface Area?

- Question
  - Why do unsupported liquid drops become nearly spherical?
- Evidence
  - Spheres have the smallest area for a fixed volume.
  - Freely suspended drops spontaneously approach spherical shapes.
- Reasoning
  - $\because$ At fixed temperature and pressure, spontaneous changes reduce total Gibbs free energy.
  - $\therefore$ Reducing interfacial area removes excess surface free energy, favoring spherical drops.
- Takeaway
  - Free-energy minimization drives area minimization.

# Why Do Liquids Have Different Surface Tensions?

- Question
  - Why is mercury's surface tension much larger than ethanol's?
- Evidence
  - Mercury: $458\,\mathrm{mN\,m^{-1}}$; water: 72; ethanol: 22.
  - Their densities differ far less than their surface tensions.
- Reasoning
  - $\because$ Surface energy reflects both attraction strength and the number of lost intermolecular contacts.
  - $\therefore$ Stronger pair potentials increase $\gamma$, but similar coordination prevents hundredfold differences.
- Takeaway
  - *Pair-potential depth* controls interfacial energy.

# Cohesion, Adhesion, and the Meniscus

## Cohesive Forces

IMFs between **identical** molecules (liquid–liquid).

Example: water molecules attract each other via H-bonds.

## Adhesive Forces

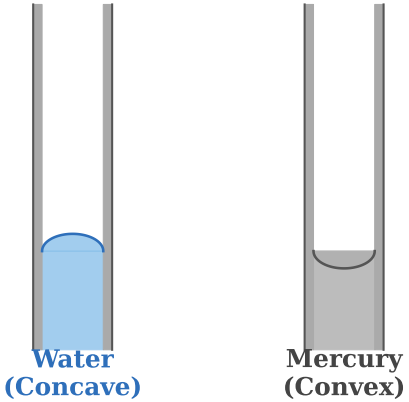
IMFs between **different** molecules (liquid–surface).

Example: water attracts glass ($SiO_2$) via H-bonds.

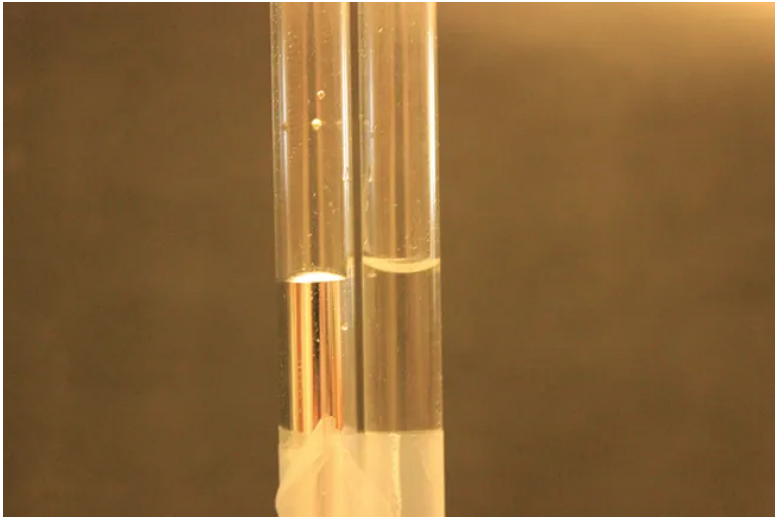
Always read a liquid volume at the **bottom** of a concave meniscus.

### Meniscus: Water vs. Mercury

*Adhesion > Cohesion* *Cohesion > Adhesion*



# Meniscus Shape Depends on Relative Strength of IMFs



# Why Does a Drop Meet a Surface at One Angle?

- Question
  - Why is the contact angle fixed by the interface, not the drop size?
- Evidence
  - Large and small drops show nearly identical contact angles.
  - The angle changes when only the solid surface changes.
- Reasoning
  - $\because$ Only three interfaces meet at the contact line, where each interfacial tension pulls tangentially.
  - $\therefore$ Horizontal force balance gives $\gamma_{sv} = \gamma_{sl} + \gamma_{lv} \cos\theta$, independent of drop volume.
- Takeaway
  - *Interfacial force balance* determines contact angle.

# What Does the Contact Angle Reveal?

- Question
  - What does the sign of $\cos\theta$ reveal about wetting?
- Evidence
  - Water on glass: $\theta \approx 0°$; water on wax: $\theta \approx 110°$.
  - Mercury on glass: $\theta \approx 140°$.
- Reasoning
  - $\because$ The contact angle adjusts until competing interfacial tensions balance at the contact line.
  - $\therefore$ Positive $\cos\theta$ indicates wetting; negative $\cos\theta$ indicates non-wetting because replacing solid–vapor becomes unfavorable.
- Takeaway
  - *Contact angle* measures competing surface free energies.

# Why Must the Meniscus Curve?

- Question
  - Why cannot a wetting liquid remain perfectly flat?
- Evidence
  - Wetting liquids form concave menisci; non-wetting liquids form convex ones.
  - Pressure measurements differ across curved liquid interfaces.
- Reasoning
  - $\because$ A curved interface creates the pressure difference needed to balance interfacial tension everywhere along the surface.
  - $\therefore$ The meniscus adopts the curvature consistent with both contact-angle and pressure equilibrium.
- Takeaway
  - Curvature links surface tension to pressure.

# Viscosity

## Definition

**Viscosity** is a liquid's resistance to flow. Units: pascal-second (Pa s) or millipascal-second (mPa s).

| Substance | Viscosity (mPa·s, 25°C) | IMF |
|---|---|---|
| Octane | 0.508 | London (nonpolar) |
| Water | 0.890 | H-bonding |
| Ethanol | 1.074 | H-bonding |
| Ethylene glycol | 16.1 | Many H-bonds |
| Honey | ∼2000–10000 | Many H-bonds + size |

**Stronger IMFs** ⇒ **higher viscosity**.
**Higher temperature** ⇒ more kinetic energy ⇒ **lower viscosity** (molecules can flow past each other more easily).

# What Microscopic Process Limits Liquid Flow?

- Question
  - Why does heating decrease liquid viscosity but increase gas viscosity?
- Evidence
  - Warm honey flows faster than cold honey.
  - Gas viscosity increases as molecular speed increases.
- Reasoning
  - $\because$ Liquid molecules must escape transient *neighbor cages*, whereas gas molecules mainly transfer momentum by collisions.
  - $\therefore$ Heating accelerates cage escape in liquids but increases momentum transport in gases.
- Takeaway
  - Rate-limiting molecular motion determines viscosity.

# Why Does Liquid Viscosity Depend Exponentially on Temperature?

- Question
  - Why does a small temperature increase dramatically reduce viscosity?
- Evidence
  - Flow requires molecules to leave their neighboring cages.
  - Only some molecules possess enough thermal energy to escape.
- Reasoning
  - $\because$ Escape requires overcoming an energy barrier set by the depth of the intermolecular pair potential.
  - $\therefore$ Escape probability follows a Boltzmann distribution, giving $\eta \propto e^{E_a/k_B T}$.
- Takeaway
  - *Activated escape* governs liquid viscosity.

# Why Does Additional Hydrogen Bonding Increase Viscosity?

- Question
  - Why is ethylene glycol far more viscous than ethanol?
- Evidence
  - Ethylene glycol contains two hydroxyl groups instead of one.
  - Its viscosity is roughly fifteen times larger than ethanol's.
- Reasoning
  - $\because$ Additional hydrogen bonds deepen the molecular cage, increasing the escape energy barrier.
  - $\therefore$ Even modest increases in barrier height greatly reduce escape frequency and increase viscosity.
- Takeaway
  - *Barrier height* controls flow resistance.

## Check Your Understanding

(a) Ethylene glycol (antifreeze) has two –OH groups per molecule; ethanol has one. Which is more viscous? Why?

(b) Motor oil is more viscous at 0 °C than at 100 °C. Is this consistent with your knowledge of IMFs and temperature?

Come to lecture to see the answer.

# Capillary Action

## Definition

**Capillary action** is the spontaneous rise (or fall) of a liquid in a narrow tube due to the interplay of adhesive and cohesive forces.

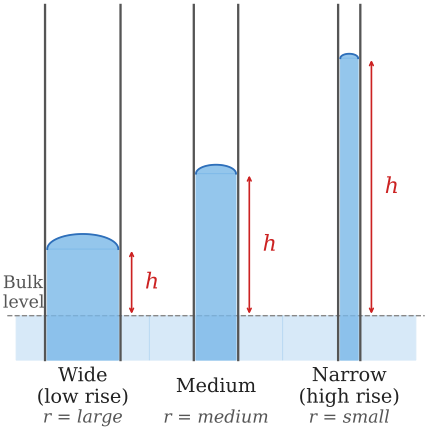
Capillary Rise Formula:

$$h = \frac{2T\cos\theta}{r\rho g}$$

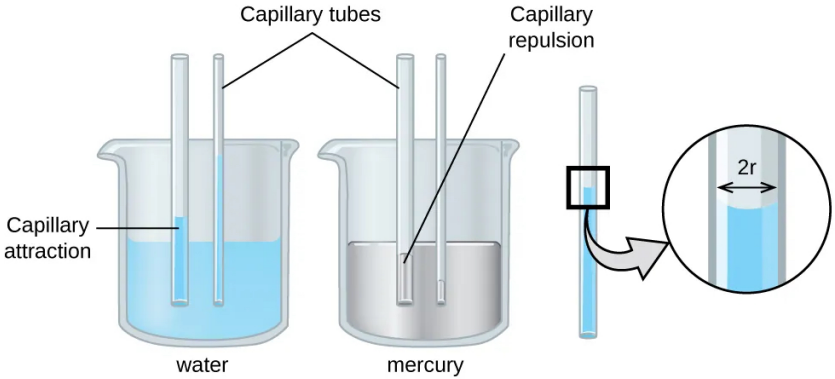
- $h$ = height of rise
- $T$ = surface tension
- $\theta$ = contact angle (water/glass: $\approx 0°$)
- $r$ = tube radius
- $\rho$ = liquid density
- $g$ = gravity

Narrower tube $\Rightarrow$ smaller $r \Rightarrow$ **greater** height of rise.
Applications: paper towels, plant xylem, blood collection tubes, chromatography.

Capillary Rise: $h = \frac{2T\cos\theta}{r\rho g}$



# Capillary Action




Depending upon the relative strengths of adhesive and cohesive forces, a liquid may rise (such as water) or fall (such as mercury) in a glass capillary tube. The extent of the rise (or fall) is directly proportional to the surface tension of the liquid and inversely proportional to the density of the liquid and the radius of the tube.

# Why Does Liquid Rise in a Narrow Tube?

- Question
  - Why does capillary rise increase as tube radius decreases?
- Evidence
  - Narrower capillaries lift liquids to greater heights.
  - Curved menisci exhibit a pressure difference across the interface.
- Reasoning
  - $\because$ Smaller meniscus curvature produces larger *Young–Laplace* pressure that pushes liquid upward.
  - $\therefore$ Rise stops when Laplace pressure balances the hydrostatic pressure of the liquid column, giving $h = \dfrac{2\gamma\cos\theta}{r\rho g}$.
- Takeaway
  - Pressure balance determines capillary height.

# Why Does Wetting Control Rise or Depression?

- Question
  - Why do non-wetting liquids sink instead of rise?
- Evidence
  - Water rises in glass capillaries.
  - Mercury forms a depressed meniscus in glass.
- Reasoning
  - $\because$ The contact angle fixes the direction of the surface-tension force through its vertical component.
  - $\therefore$ $\cos\theta > 0$ lifts the liquid, whereas $\cos\theta < 0$ reverses the force and depresses the column.
- Takeaway
  - *Contact angle* determines force direction.

# Why Is Capillarity Alone Insufficient for Tall Trees?

- Question
  - Can capillary action alone raise water 100 m in xylem?
- Evidence
  - A 100 m rise requires micrometer-scale capillary radii.
  - Actual xylem vessels are generally much wider.
- Reasoning
  - $\because$ Larger radii produce smaller Laplace pressures, limiting capillary support against gravity.
  - $\therefore$ Trees require additional negative pressure from *transpiration* to sustain tall water columns.
- Takeaway
  - Pressure sources combine to transport water.

# Example: Capillary Rise

## Water in a Glass Capillary — (chem2e ch10)

Water rises in a glass capillary tube with radius 0.25 mm at 25 °C.
Given: $T = 71.99\,\frac{\mathrm{mN}}{\mathrm{m}}$, $\theta \approx 0°$, $\rho = 997\,\frac{\mathrm{kg}}{\mathrm{m}^3}$, $g = 9.8\,\frac{\mathrm{m}}{\mathrm{s}^2}$.
How high does the water rise?

$$h = \frac{2\,T\cos\theta}{r\rho g}$$

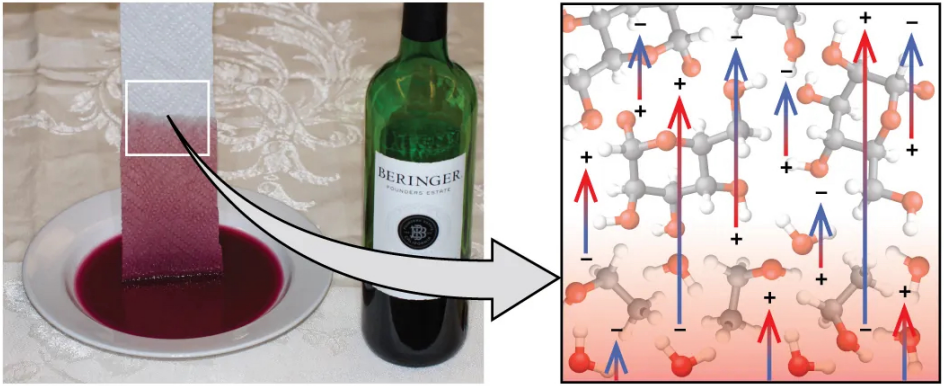
$$h = \frac{2 \times 0.071\,99\,\frac{\mathrm{N}}{\mathrm{m}} \times \cos(0°)}{2.5 \times 10^{-4}\,\mathrm{m} \times 997\,\frac{\mathrm{kg}}{\mathrm{m}^3} \times 9.8\,\frac{\mathrm{m}}{\mathrm{s}^2}}$$

$$\boxed{h \approx 0.059\,\mathrm{m} = 5.9\,\mathrm{cm}}$$

$\cos(0°) = 1$ (water fully wets glass).

Narrowing the tube by 10× would raise water 10× higher.

# Example: Capillary Action: Wine + Towel




Wine wicks up a paper towel (left) because water and ethanol molecules are strongly attracted to the −OH groups on the towel's cellulose fibers, while water molecules are also strongly attracted to neighboring water (and ethanol) molecules (right).

# Example: Capillary Action: Blood in Thin Vial

Blood is collected for medical analysis by capillary action, which draws blood into a narrow glass tube without the need for pumping or suction. The blood rises because it is attracted to the glass surface and to neighboring blood molecules.

# Part III

# Phase Transitions

# Outline of Part III: Phase Transitions

Phase Transitions

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Phase Transitions

# Overview: Phase Transitions

A **phase transition** is a change from one state of matter to another.

| Transition | From | To | Energy |
|---|---|---|---|
| Melting (fusion) | solid | liquid | endothermic |
| Freezing | liquid | solid | exothermic |
| Vaporization | liquid | gas | endothermic |
| Condensation | gas | liquid | exothermic |
| Sublimation | solid | gas | endothermic |
| Deposition | gas | solid | exothermic |

Energy is **required** to *separate* molecules (endothermic = breaking IMFs).
Energy is **released** when molecules *join* (exothermic = forming IMFs).

# Phase Transitions: Relative Energy in Each Phase

The intermolecular potential energy for a given substance depends on the phase:

$$E_{\text{solid}} < E_{\text{liquid}} < E_{\text{gas}}$$

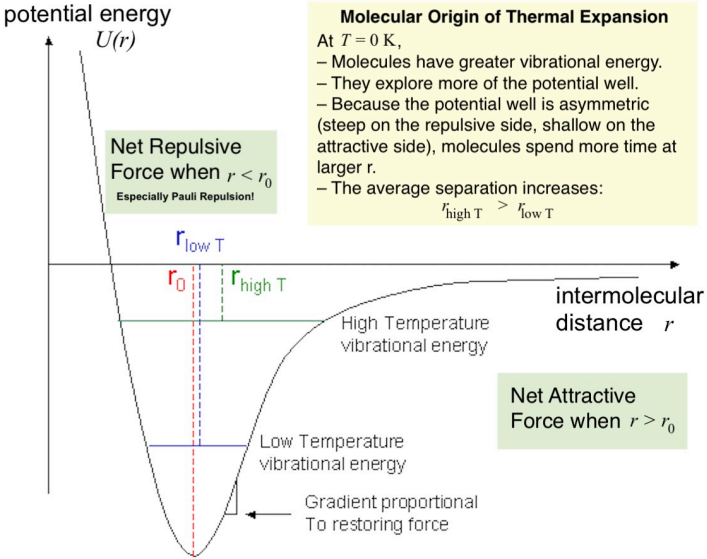
$\therefore$ going from a lower-energy phase (on the left) to a higher-energy phase (on the right) requires an input of energy (i.e. an endothermic process).

**Example: Solid $\rightarrow$ Gas**

$$E_{\text{solid}} \rightarrow E_{\text{gas}}$$

Requires energy $\because$ the solid phase has less energy than the gas phase. *Sublimating* the solid $\therefore$ is an *endothermic* process.

# Intermolecular Potential-Energy Curve for Condensed Matter




**Molecular Origin of Thermal Expansion**

At $T = 0$ K,
– Molecules have greater vibrational energy.
– They explore more of the potential well.
– Because the potential well is asymmetric (steep on the repulsive side, shallow on the attractive side), molecules spend more time at larger r.
– The average separation increases:

$$r_{\text{high T}} > r_{\text{low T}}$$

Intermolecular potential energy curve illustrating molecular motion in condensed phases (solids and liquids).

- In **solids**, atoms vibrate about their equilibrium separation within the potential well.
- In **liquids**, molecules remain within the attractive well *on average* but are free to diffuse between neighboring positions and exhibit significant translational and rotational motion in addition to vibration.

# Why Does Intermolecular Potential Energy Have a Minimum?

- Question
  - Why do molecules have an equilibrium separation instead of continually approaching or separating?
- Evidence
  - Molecules in condensed phases maintain nearly fixed nearest-neighbor distances.
  - Compressing or separating molecules requires external work.
- Reasoning
  - $\because$ Electron-cloud overlap causes strong repulsion, while longer-range intermolecular attractions lower potential energy.
  - $\therefore$ Their competition creates an *energy minimum*; solids, liquids, and gases occupy progressively higher regions of the well.
- Takeaway
  - Phase changes climb the intermolecular energy well.

# Why Does Vaporization Require *So Much* Energy?

- Question
  - Why is vaporization much more endothermic than melting?
- Evidence
  - Melting preserves many neighboring molecular contacts.
  - Vaporization separates molecules until intermolecular attractions vanish.
- Reasoning
  - $\because$ Escaping to the gas requires climbing nearly *the entire* intermolecular potential well created by *many* neighbors.
  - $\therefore$ $\Delta H_{\text{vap}}$ remains far below chemical bond energies because *intermolecular* wells are much shallower than *intramolecular* wells.
- Takeaway
  - The depth of the intermolecular-potential-energy well determines phase-transition enthalpy.

# Why Does Sublimation Equal Fusion Plus Vaporization?

- Question
  - Why is sublimation the sum of melting and vaporization enthalpies?
- Evidence
  - Sublimation and two-step melting–vaporization reach the same final gas state.
  - Measured values agree closely at the same temperature.
- Reasoning
  - $\because$ Enthalpy depends only on initial and final states, not the transformation pathway.
  - $\therefore \Delta H_{\text{sub}} = \Delta H_{\text{fus}} + \Delta H_{\text{vap}}$; temperature changes alter each term through heat capacities, especially vaporization.
- Takeaway
  - State functions connect all phase transitions.

# Vapor Pressure

## Definition

**Vapor pressure** is the pressure exerted by a vapor in equilibrium with its liquid (or solid) in a closed container at a given temperature.

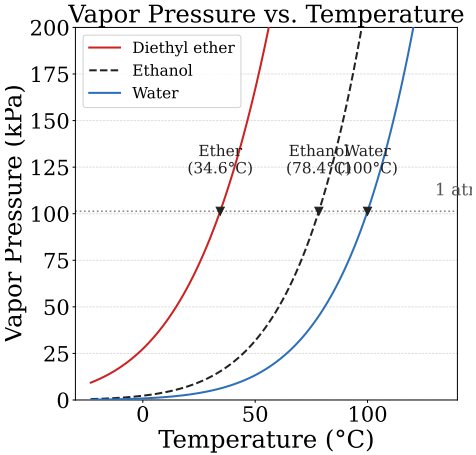
## Dynamic Equilibrium

In a closed container, vaporization and condensation eventually reach the **same rate**:

$$\text{liquid} \rightleftharpoons \text{gas}$$

The vapor pressure depends on **temperature** and the **strength of IMFs**.

**Weaker IMFs** ⇒ easier to escape ⇒ **higher** vapor pressure.
**Higher temperature** ⇒ more molecules have enough KE to escape ⇒ **higher** vapor pressure.



# Why Does a Liquid Produce Vapor?

- Question
  - Why do molecules escape a liquid below its boiling point?
- Evidence
  - Water forms vapor at 298 K in a sealed container.
  - Most molecules remain liquid despite continuous evaporation.
- Reasoning
  - $\because$ Molecular collisions create a *Maxwell–Boltzmann distribution*; only the energetic tail exceeds the intermolecular binding that makes the substance a liquid.
  - $\therefore$ Escape is continuous because a small, constantly renewed fraction crosses the surface energy barrier.
- Takeaway
  - Energy distributions govern molecular escape.

# Why Do Only Some Molecules Escape?

- Question
  - Why does only a small fraction of surface molecules evaporate?
- Evidence
  - Molecules continually exchange kinetic energy through collisions.
  - Water requires about 40 kJ $\text{mol}^{-1}$ to escape its intermolecular *potential well*.
- Reasoning
  - $\because$ Collisions produce a range of kinetic energies, but only molecules exceeding the well depth can escape.
  - $\therefore$ Deeper potential wells leave exponentially fewer molecules able to evaporate: $e^{-\Delta H_{\text{vap}}/RT}$.
- Takeaway
  - Potential well depth controls the escaping fraction.

# Why Is There Only One Vapor Pressure at Each Temperature?

- Question
  - Why does vapor pressure depend only on temperature? Why does it *not* depend on how much liquid or space there is?
- Evidence
  - Vapor pressure returns to the same value after expansion or compression.
  - This occurs whenever both liquid and vapor remain present.
- Reasoning
  - Temperature fixes the escaping fraction, while vapor density controls how often molecules condense back into the liquid.
  - $\therefore$ If pressure is too low, evaporation exceeds condensation; if too high, condensation exceeds evaporation, restoring one equilibrium pressure.
- Takeaway
  - Vapor density adjusts until evaporation equals condensation, making vapor density a *dynamic-equilibrium property*.

# What Happens at Dynamic Equilibrium?

- Question
  - Why is there no net evaporation despite continual molecular exchange?
- Evidence
  - Roughly $10^{22}$ water molecules cross each $cm^2$ each second in each direction.
  - Liquid amount remains constant after equilibrium is established.
- Reasoning
  - Surface escape and vapor collisions occur simultaneously with equal opposing molecular fluxes.
  - $\therefore$ Large instantaneous exchanges produce zero net mass transfer at equilibrium.
- Takeaway
  - Equal opposing fluxes create dynamic equilibrium.

# Boiling Point

## Definition

**Boiling** occurs when a liquid's vapor pressure equals the external (atmospheric) pressure. Bubbles of vapor form throughout the liquid.

## Normal Boiling Point

The **normal boiling point** is the temperature at which vapor pressure equals exactly 101.3 kPa (1 atm).

- At **high altitude** (lower $P_{atm}$), water boils below 100 °C.
  *e.g. at Denver (1.6 km), water boils at ≈ 94 °C — eggs take longer to cook.*
- In a **pressure cooker** (higher $P$), water boils above 100 °C — food cooks faster.

Boiling is **not** the same as evaporation. Evaporation occurs at any temperature from the surface; boiling occurs throughout the liquid at a specific temperature.

# Why Does Boiling Begin at One Temperature?

- Question
  - Why can evaporation occur anytime, but boiling begins only at a specific temperature?
- Evidence
  - Liquids *evaporate* below their boiling point.
  - Bulk *vapor-bubbles* only appear near the boiling point.
- Reasoning
  - Surface molecules escape individually, whereas bulk bubbles must resist the surrounding liquid pressure.
  - $\therefore$ Boiling begins only when vapor pressure can support stable bubble growth.
- Takeaway
  - Boiling requires *stable* vapor bubbles, not merely escaping molecules.

# Why Are Small Bubbles Unstable?

- Question
  - Why do tiny vapor bubbles collapse before growing?
- Evidence
  - A bubble of radius $r$ and surface tension $\gamma$ experiences an inward *Laplace pressure* $2\gamma/r$.
  - Smaller bubbles experience larger inward pressure.
- Reasoning
  - $\because$ Surface tension compresses curved interfaces, requiring higher internal vapor pressure for expansion.
  - $\therefore$ Tiny bubbles need extra heating before stable growth becomes possible.
- Takeaway
  - Surface tension delays bubble growth.

# Why Can Water Become Superheated?

- Question
  - Why can microwave-heated water boil violently after disturbance?
- Evidence
  - Smooth containers often heat water above its normal boiling temperature.
  - Disturbance suddenly creates vigorous bubbling.
- Reasoning
  - $\because$ Without nucleation sites, only tiny unstable bubbles form despite continued heating.
  - $\therefore$ Disturbance creates larger bubbles that exceed the stability threshold and rapidly expand.
- Takeaway
  - Bubble nucleation controls boiling onset.

# Why Does a Pressure Cooker Cook Faster?

- Question
  - Why does using a pressure cooker to increase pressure shorten cooking time?
- Evidence
  - Water boils near 100°C at atmospheric pressure.
  - Pressure cookers operate above atmospheric pressure.
  - Inside a pressure cooker, water remains liquid above 100°C.
- Reasoning
  - Higher pressure requires a higher vapor pressure before boiling begins, allowing the liquid to reach a higher temperature.
  - $\therefore$ Food in the cooker reaches a higher temperature, so the chemical reactions responsible for cooking proceed faster.
- Takeaway
  - Higher boiling temperature accelerates cooking reactions.

# The Clausius-Clapeyron Equation

## Vapor Pressure and Temperature

Vapor pressure increases **exponentially** with temperature:

$$\ln P = -\frac{\Delta H_{\text{vap}}}{R} \cdot \frac{1}{T} + \ln A$$

## Two-Point Form — (**Most Useful for Calculations**)

$$\ln\left(\frac{P_2}{P_1}\right) = \frac{\Delta H_{\text{vap}}}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

- $P_1$, $P_2$ = vapor pressures at temperatures $T_1$, $T_2$ (in K)
- $\Delta H_{\text{vap}}$ = enthalpy of vaporization ($\frac{\text{J}}{\text{mol}}$)
- $R = 8.314\ \frac{\text{J}}{\text{mol K}}$

Always convert temperatures to **Kelvin**! The equation fails with Celsius.

# Why Does Every Phase Boundary Have a Slope?

- Question
  - Why must pressure change with temperature to preserve phase coexistence?
- Evidence
  - The *chemical potential* $\mu$ is the molar Gibbs free energy that determines a phase's escaping tendency.
  - At coexistence, $\mu_l = \mu_g$, so neither phase grows at the other's expense.
- Reasoning
  - $\because$ *Entropy* measures the number of accessible molecular arrangements, while pressure acts through molar volume; these change $\mu$ differently for liquid and vapor.
  - $\therefore$ Pressure must change with temperature to maintain $\mu_l = \mu_g$, giving $\frac{dP}{dT} = \frac{\Delta S}{\Delta V}$.
- Takeaway
  - Phase boundaries balance entropy and volume to equalize chemical potentials.

# Why Does Vapor Pressure Rise Exponentially?

- Question
  - Why does the liquid–gas boundary become the Clausius–Clapeyron equation?
- Evidence
  - Gas volume greatly exceeds liquid volume far from the critical point.
  - Vapor behaves approximately as an *ideal gas*.
- Reasoning
  - Nearly all expansion occurs in the vapor, whose volume grows from molecular translational motion.
  - $\therefore$ Integrating the Clapeyron slope yields the exponential Clausius–Clapeyron relation.
- Takeaway
  - Exponential behavior reflects gas expansion.

# Why Does the Approximation Eventually Fail?

- Question
  - Why does Clausius–Clapeyron fail near the critical point?
- Evidence
  - Liquid and vapor densities become increasingly similar near the critical point.
  - The coexistence curve no longer follows a simple exponential trend.
- Reasoning
  - $\because$ The phase-volume difference shrinks until liquid and vapor become physically indistinguishable.
  - $\therefore$ The large-volume approximation collapses, invalidating the integrated equation.
- Takeaway
  - Approximations fail as phases converge.

# Why Does $\Delta H_{\text{vap}}$ Decrease with Temperature?

- Question
  - Why is the enthalpy of vaporization smaller at higher temperatures?
- Evidence
  - Water has $\Delta H_{\text{vap}} \approx 44.8$ kJ mol$^{-1}$ near room temperature.
  - At 100°C, $\Delta H_{\text{vap}} \approx 40.7$ kJ mol$^{-1}$.
- Reasoning
  - Thermal motion already lifts molecules higher within intermolecular potential wells before evaporation.
  - $\therefore$ Less additional energy is needed for a molecule to escape as $T$ increases.
- Takeaway
  - Thermal energy reduces remaining escape energy.

# Example: Clausius-Clapeyron Equation

## Vapor Pressure of Water — (chem2e ch10)

The vapor pressure of water is 1.94 kPa at 17 °C and 3.61 kPa at 27 °C. Calculate $\Delta H_{\text{vap}}$ for water.

$T_1 = 290\,\text{K},\ T_2 = 300\,\text{K}$

$$\ln\left(\frac{3.61}{1.94}\right) = \frac{\Delta H_{\text{vap}}}{8.314\,\frac{\text{J}}{\text{mol K}}}\left(\frac{1}{290} - \frac{1}{300}\right)$$

$$0.620 = \frac{\Delta H_{\text{vap}}}{8.314} \times 1.149 \times 10^{-4}$$

$$\boxed{\Delta H_{\text{vap}} \approx 4.48 \times 10^{4}\,\frac{\text{J}}{\text{mol}} = 44.8\,\frac{\text{kJ}}{\text{mol}}}$$

Literature value: $44.0\,\frac{\text{kJ}}{\text{mol}}$ at 25 °C.

Good agreement! Small temperature range limits precision.

## Check Your Understanding

Which of the following has the **highest** vapor pressure at room temperature?

(a) Diethyl ether (weak IMFs, low BP)
(b) Ethanol (H-bonding, moderate BP)
(c) Water (strong H-bonding, BP = 100°C)

Which one is most **volatile** (evaporates fastest)?

Come to lecture to see the answer.

# Enthalpy of Phase Transitions

| Quantity | Symbol | Value for Water |
|---|---|---|
| Enthalpy of vaporization | $\Delta H_{\text{vap}}$ | $40.67\,\frac{\text{kJ}}{\text{mol}}$ at $100\,^{\circ}\text{C}$ |
| Enthalpy of fusion | $\Delta H_{\text{fus}}$ | $6.01\,\frac{\text{kJ}}{\text{mol}}$ at $0\,^{\circ}\text{C}$ |
| Enthalpy of sublimation | $\Delta H_{\text{sub}}$ | $51.1\,\frac{\text{kJ}}{\text{mol}}$ (ice at $-10^{\circ}\text{C}$) |

$\Delta H_{\text{sub}} \approx \Delta H_{\text{fus}} + \Delta H_{\text{vap}}$
(sublimation = melting + vaporization in sequence)

## Practical Application: Perspiration

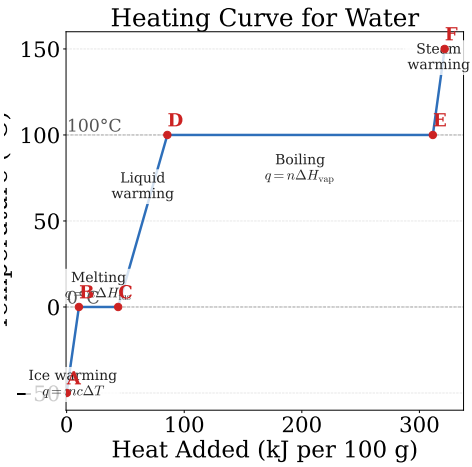
The body absorbs 40.67 kJ of heat for every mole (18 g) of sweat that evaporates from the skin — a very effective cooling mechanism.

# Heating Curves

## For 1 g of Water, Ice → Steam

- **Segment A–B**: ice warming; $q = mc\Delta T$, $c_{\text{ice}} = 2.09\ \frac{\text{J}}{\text{g K}}$
- **B–C**: melting (plateau at 0 °C); $q = n\Delta H_{\text{fus}}$
- **C–D**: liquid water warming; $c_{\text{liq}} = 4.18\ \frac{\text{J}}{\text{g K}}$
- **D–E**: boiling (plateau at 100 °C); $q = n\Delta H_{\text{vap}}$
- **E–F**: steam warming; $c_{\text{gas}} = 2.01\ \frac{\text{J}}{\text{g K}}$

During phase transitions (plateaus), temperature **does not change** because energy goes into breaking IMFs.



# Why Is Vaporization Much More Energetic Than Melting?

- Question
  - Why is $\Delta H_{\text{vap}}$ much larger than $\Delta H_{\text{fus}}$?
- Evidence
  - Water: $\Delta H_{\text{fus}} \approx 6.0$ kJ mol$^{-1}$.
  - Water: $\Delta H_{\text{vap}} \approx 40.7$ kJ mol$^{-1}$.
- Reasoning
  - Melting breaks only enough intermolecular contacts for molecular rearrangement.
  - $\therefore$ Vaporization separates molecules completely, overcoming nearly all attractive interactions.
- Takeaway
  - Broken interactions determine transition enthalpy.

# Why Does Temperature Remain Constant During a Phase Change?

- Question
  - Why does heating stop raising temperature during melting or boiling?
- Evidence
  - Heating curves show horizontal plateaus during phase transitions.
  - Heat continues entering the sample throughout each plateau.
- Reasoning
  - Added energy raises molecular *potential energy* by separating molecules, not their kinetic energy.
  - $\therefore$ Heat changes phase fraction until coexistence ends, while temperature remains unchanged.
- Takeaway
  - Phase changes store heat as potential energy.

# Why Does *Liquid* Water Have the Largest Heat Capacity?

- Question
  - Why does *liquid* water require more heat per $\Delta T$ than ice or steam even though ice has the most hydrogen bonds?
- Evidence
  - Ice has a rigid hydrogen-bond network; steam has almost none.
  - Liquid water continually breaks and reforms *hydrogen bonds* and has the highest specific heat capacity.
- Reasoning
  - Heating increases molecular motion.
  - $\because$ liquid molecules can continually reorganize their *hydrogen-bond* network, added energy changes both molecular motion and intermolecular *potential energy*
  - $\therefore$ more heat is required for each degree of temperature increase, predicting higher heat capacities when intermolecular rearrangement is extensive.
- Takeaway
  - Dynamic intermolecular rearrangement stores thermal energy.

# Why Does Temperature Stop Increasing During a Phase Change?

- Question
  - Why does adding heat stop raising temperature during melting or boiling?
- Evidence
  - Heat continues entering the sample throughout each heating-curve plateau.
  - During the plateau, the fraction of each phase changes while temperature remains constant.
- Reasoning
  - $\because$ Molecules must gain enough energy to move farther apart against *intermolecular forces*, added heat increases *intermolecular potential energy* instead of average molecular kinetic energy
  - $\therefore$ temperature remains constant until sufficient molecules escape their original arrangement, predicting a plateau whenever a phase change occurs.
- Takeaway
  - Phase changes store energy as intermolecular potential energy.

# Example: Heating Curve Calculation

## Energy to Convert Ice to Steam

How much heat (in kJ) is required to convert 100 g of ice at −20 °C to steam at 120 °C?
Use: $\Delta H_{\text{fus}} = 6.01\ \frac{\text{kJ}}{\text{mol}}$; $\Delta H_{\text{vap}} = 40.67\ \frac{\text{kJ}}{\text{mol}}$; $MW(\text{H}_2\text{O}) = 18.0\ \frac{\text{g}}{\text{mol}}$.

$$q_1 = mc\Delta T = 100\,\text{g} \times 2.09\ \frac{\text{J}}{\text{g K}} \times 20\,\text{K} = 4.18\,\text{kJ}$$

$$q_2 = n\Delta H_{\text{fus}} = \frac{100}{18.0}\,\text{mol} \times 6.01\ \frac{\text{kJ}}{\text{mol}} = 33.4\,\text{kJ}$$

$$q_3 = mc\Delta T = 100\,\text{g} \times 4.18\ \frac{\text{J}}{\text{g K}} \times 100\,\text{K} = 41.8\,\text{kJ}$$

$$q_4 = n\Delta H_{\text{vap}} = \frac{100}{18.0}\,\text{mol} \times 40.67\ \frac{\text{kJ}}{\text{mol}} = 226\,\text{kJ}$$

$$q_5 = mc\Delta T = 100\,\text{g} \times 2.01\ \frac{\text{J}}{\text{g K}} \times 20\,\text{K} = 4.02\,\text{kJ}$$

$$\boxed{q_{\text{total}} = 4.18 + 33.4 + 41.8 + 226 + 4.02 = 309\,\text{kJ}}$$

## Check Your Understanding

Looking at the heating curve for water:

(a) Why does the temperature remain constant during melting and boiling?

(b) The boiling plateau is much longer than the melting plateau. What does this tell you about $\Delta H_{\text{vap}}$ vs. $\Delta H_{\text{fus}}$?

Come to lecture to see the answer.

# Sublimation and Deposition

## Definitions

- **Sublimation**: direct transition from **solid** $\rightarrow$ **gas** (endothermic).
- **Deposition**: direct transition from **gas** $\rightarrow$ **solid** (exothermic).

## Dry Ice ($CO_2$)

$CO_2$ sublimes at $-78.5\,^{\circ}\mathrm{C}$ at $1\,\mathrm{atm}$ (no liquid phase at normal pressure).

Used in fog machines, food preservation, and refrigeration.

## Frost / Freeze-Drying

Frost forms by deposition of water vapor directly onto cold surfaces.

Freeze-drying preserves food by sublimating ice at low pressure — no liquid water $\Rightarrow$ no structural damage to food.

# Part IV

# Phase Diagrams

# Outline of Part IV: Phase Diagrams

Phase Diagrams

# Outline of Part IV: Phase Diagrams

Phase Diagrams

# Phase Diagrams

## Definition

A **phase diagram** is a graph of pressure (y-axis) vs. temperature (x-axis) that shows the physical state of a substance under given conditions and the boundaries between phases.

## Key Features

- **Regions**: areas where solid, liquid, or gas is the stable phase.
- **Curves**: boundaries where two phases coexist in equilibrium.
- **Triple point**: the unique T and P where all three phases coexist.
- **Critical point**: the T and P above which distinct liquid and gas phases cannot exist; above this point a **supercritical fluid** forms.

# What Determines Whether Molecules Change Phase?

- Question
  - What decides whether molecules remain in one phase or move into another?
- Evidence
  - At *dynamic equilibrium*, molecules continuously move between phases.
  - No phase grows overall while temperature and pressure remain constant.
- Reasoning
  - Molecules spontaneously move toward lower *chemical potential*. Equilibrium requires no preferred direction, so every phase has the same chemical potential. Pressure and temperature determine that potential for a pure substance.
  - $\therefore$ equilibrium is completely specified by these two *intensive variables*, $P$ and $T$.
- Takeaway
  - Equal chemical potential defines phase equilibrium.

# The Gibbs Phase Rule: Predicting Phase Diagram Geometry

$$\boxed{F = C - P + 2}$$

- $F =$ degrees of freedom (number of intensive variables that can be chosen independently)
- $C =$ number of chemically independent *components*
- $P =$ number of *phases in equilibrium*
- The "+2" corresponds to the two intensive variables, pressure ($P$) and temperature ($T$)

## Example: Pure water with liquid and vapor in equilibrium

- $C = 1$ (one *component*: $H_2O$)
- $P = 2$ (liquid and vapor)
- $F = 1 - 2 + 2 = 1$
- Once either $P$ or $T$ is specified, the other is fixed by equilibrium.

# Why Can a Phase Diagram Be Drawn?

- Question
  - Why are only pressure and temperature needed to map phase equilibrium?
- Evidence
  - A pure substance has one composition.
  - Phase equilibrium requires equal *chemical potential* in every coexisting phase.
- Reasoning
  - $\because$ Equality of chemical potential removes one independent variable for each additional phase, leaving only unconstrained *intensive variables*; $\therefore$ the Gibbs phase rule, $F = C - P + 2$, predicts how many variables must be specified and why a pure-substance phase diagram has pressure and temperature as its axes.
- Takeaway
  - Phase-rule constraints determine phase-diagram dimensions.

# Why Is the Triple Point a Single Point?

- Question
  - Why does three-phase equilibrium occur at only one pressure and temperature?
- Evidence
  - For one component with three phases, $F = 1 - 3 + 2 = 0$.
  - Every phase must simultaneously satisfy identical equilibrium conditions.
- Reasoning
  - $\because$ Three equilibrium constraints exhaust every remaining independent intensive variable.
  - $\therefore$ Any change in pressure or temperature destroys three-phase coexistence.
- Takeaway
  - Zero freedom creates a unique state.

# Why Are Coexistence Boundaries Curves?

- Question
  - Why do two phases coexist along curves instead of regions?
- Evidence
  - For one component with two phases, $F = 1 - 2 + 2 = 1$.
  - The *Clapeyron equation* gives $dP/dT$ along coexistence.
- Reasoning
  - $\because$ One remaining degree of freedom allows pressure to adjust uniquely as temperature changes.
  - $\therefore$ Two-phase equilibrium traces a continuous curve with a definite slope.
- Takeaway
  - One freedom generates a coexistence curve.

# How Does the Phase Rule Organize Every Phase Diagram?

- Question
  - How do regions, curves, and points follow one governing principle?
- Evidence
  - Single-phase states occupy regions.
  - Two- and three-phase equilibria appear as curves and points.
- Reasoning
  - $\because$ Each additional equilibrium phase introduces another constraint on independent variables.
  - $\therefore$ Geometry reflects the remaining degrees of freedom predicted by the Gibbs phase rule.
- Takeaway
  - Phase-diagram geometry encodes thermodynamic constraints.

# Phase Diagram: Water

## Key Data for $H_2O$

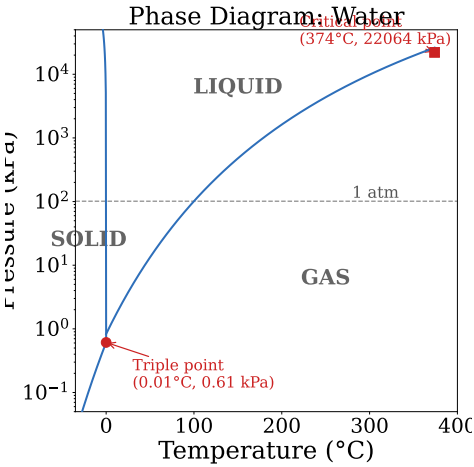
- **Triple point**: 0.01 °C, 0.611 kPa
- **Critical point**: 374 °C, 22.064 kPa
- **Normal melting point**: 0 °C at 101.3 kPa
- **Normal boiling point**: 100 °C at 101.3 kPa

## Unusual Feature

Water's **solid-liquid boundary slopes to the left** (negative slope): increasing pressure *lowers* the melting point.

Reason: ice is *less dense* than liquid water (ice floats).

This is rare among substances.



# Why Does Water Shrink When It Melts?

- Question
  - Why is $\Delta V_{\text{fus}} < 0$ for water but usually positive for other substances?
- Evidence
  - Ice is less dense than liquid water.
  - Ice forms four directional *hydrogen bonds* in a tetrahedral arrangement.
- Reasoning
  - $\because$ Tetrahedral bonding fixes molecules into an open lattice containing substantial empty space.
  - $\therefore$ Melting collapses this network, decreasing volume despite increasing molecular disorder.
- Takeaway
  - Bond geometry determines phase density.

# Why Does Water's Melting Curve Slope Downward?

- Question
  - Why does increasing pressure lower water's melting temperature?
- Evidence
  - Melting increases entropy, so $\Delta S_{\text{fus}} > 0$.
  - Water contracts on melting, so $\Delta V_{\text{fus}} < 0$.
- Reasoning
  - $\because$ Pressure favors the phase occupying less volume, making liquid thermodynamically preferred.
  - $\therefore$ The Clapeyron slope is negative, so higher pressure lowers the melting point.
- Takeaway
  - Pressure favors lower-volume phases.

# How Large Is the Pressure Effect?

- Question
  - Is blade pressure sufficient to melt ice during skating?
- Evidence
  - Clapeyron predicts only about 0.007 K melting-point change near atmospheric pressure.
  - Skating occurs even at temperatures far below this shift.
- Reasoning
  - $\because$ Ordinary pressure changes alter the equilibrium temperature only slightly.
  - $\therefore$ Pressure melting alone cannot explain the low friction experienced by skaters.
- Takeaway
  - Quantitative predictions test physical explanations.

# Why Does Water Have Many Ice Structures?

- Question
  - Why do new ice phases appear at very high pressures?
- Evidence
  - Nearly twenty crystalline ice polymorphs are known.
  - High pressure favors denser molecular arrangements.
- Reasoning
  - $\because$ Compression eventually outweighs the preference for the open tetrahedral hydrogen-bond network.
  - $\therefore$ Water adopts new crystal geometries with higher density and different bonding arrangements.
- Takeaway
  - Crystal structure balances bonding and compression.

# Phase Diagram: Carbon Dioxide

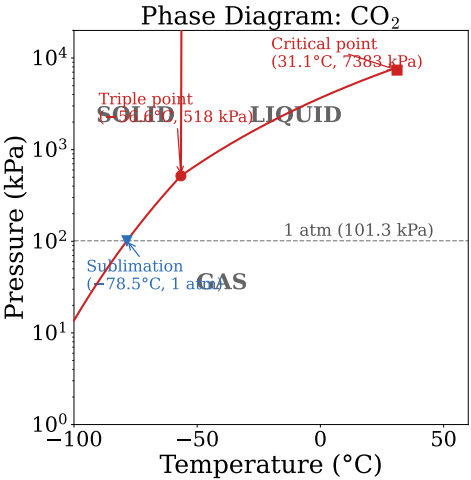
## Key Data for $CO_2$

- **Triple point**: $-56.6\,°C$, $517\,kPa$ ($5.11\,atm$)
- **Critical point**: $31.1\,°C$, $7383\,kPa$ ($72.8\,atm$)
- At $1\,atm$, $CO_2$ **sublimes** at $-78.5\,°C$

## Why Dry Ice Sublimes

The triple point of $CO_2$ lies *above* $1\,atm$. At atmospheric pressure, liquid $CO_2$ cannot exist — $CO_2$ goes directly from solid to gas.

**Solid-liquid boundary**: positive slope ($CO_2$ is normal — solid is denser than liquid).



# Why Does Dry Ice Sublime at 1 atm?

- Question
  - Why is liquid $CO_2$ absent at atmospheric pressure while liquid water is stable?
- Evidence
  - $CO_2$ has weak *dispersion forces*; water forms strong hydrogen bonds.
  - $CO_2$ triple point is 5.11 atm, whereas water's is 0.006 atm.
- Reasoning
  - $\because$ Weaker intermolecular attractions require greater pressure to keep molecules close enough for a liquid.
  - $\therefore$ At 1 atm, $CO_2$ crosses only the solid–gas boundary and sublimes.
- Takeaway
  - Attraction strength determines liquid stability.

# When Does Liquid $CO_2$ Exist?

- Question
  - Why does increasing pressure produce liquid $CO_2$?
- Evidence
  - Liquid $CO_2$ appears only above the triple-point pressure.
  - Compressed $CO_2$ is widely used in fire extinguishers.
- Reasoning
  - $\because$ Compression reduces intermolecular separation until attractive forces stabilize a condensed liquid.
  - $\therefore$ Pressurized containers maintain liquid $CO_2$, which rapidly vaporizes after release.
- Takeaway
  - Pressure stabilizes condensed phases.

# Why Is Sublimation the Only Path Below the Triple Point?

- Question
  - Why must a solid sublime instead of melting below its triple-point pressure?
- Evidence
  - Phase diagrams show no liquid region below the triple-point pressure.
  - Solids nevertheless slowly lose mass by sublimation.
- Reasoning
  - $\because$ No pressure-temperature condition stabilizes the liquid, so only solid and vapor can coexist.
  - $\therefore$ Molecules escape directly from the solid surface into the gas phase.
- Takeaway
  - Stable phases determine allowed transitions.

# Why Does Freeze-Drying Accelerate Sublimation?

- Question
  - Why does reducing pressure greatly speed freeze-drying?
- Evidence
  - Freeze-drying removes water under vacuum from frozen samples.
  - Gentle heating is applied while the material remains frozen.
- Reasoning
  - $\because$ Low vapor pressure above the surface reduces molecular return, while added heat supplies escape energy.
  - $\therefore$ Net sublimation increases without passing through the liquid phase.
- Takeaway
  - Flux imbalance controls phase-change rate.

# Supercritical Fluids

## Definition

Above the **critical temperature** and **critical pressure**, a substance exists as a **supercritical fluid** — with properties intermediate between liquid and gas:

### Like a Liquid

- High density
- Can dissolve substances

### Like a Gas

- Low viscosity
- Low surface tension
- Diffuses rapidly

### Supercritical $CO_2$ Applications

- **Decaffeination**: sc-$CO_2$ selectively dissolves and removes caffeine from coffee beans.
- **Dry cleaning**: non-toxic alternative to perchloroethylene.
- **Pharmaceutical extraction**: isolates active compounds from plants.

# Why Do Liquid and Gas Merge?

- Question
  - Why do liquid and gas become one phase above the critical temperature?
- Evidence
  - Above the critical point, density changes continuously during compression.
  - No boiling interface or latent heat is observed.
- Reasoning
  - $\because$ Thermal motion becomes comparable to the *pair-potential* well depth, preventing persistent molecular clustering.
  - $\therefore$ Compression changes density smoothly instead of producing separate liquid and gas phases.
- Takeaway
  - Stable phases require persistent intermolecular binding.

# Why Is There No Solid–Liquid Critical Point?

- Question
  - Why can liquid and gas merge continuously, but solid and liquid cannot?
- Evidence
  - Solids possess long-range *crystal order*; liquids do not.
  - Melting always changes the material's structural symmetry.
- Reasoning
  - $\because$ Long-range positional order cannot disappear continuously without destroying the crystal structure.
  - $\therefore$ Solid and liquid remain separated by a true phase boundary at every pressure.
- Takeaway
  - Structural symmetry distinguishes solids fundamentally.

# Why Is Supercritical $CO_2$ an Effective Solvent?

- Question
  - Why can supercritical $CO_2$ dissolve materials yet flow like a gas?
- Evidence
  - Supercritical $CO_2$ extracts caffeine and cleans delicate materials.
  - It has liquid-like density and gas-like viscosity.
- Reasoning
  - $\because$ High density supplies frequent molecular contacts, while weak intermolecular resistance allows rapid transport.
  - $\therefore$ Solutes dissolve efficiently and diffuse quickly through complex materials.
- Takeaway
  - Transport and solvation arise from different properties.

# What Unifies the Entire Phase Diagram?

- Question
  - What determines whether distinct phases can exist?
- Evidence
  - Phase boundaries disappear only for the liquid–gas transition.
  - Solid phases remain separated from fluids throughout the phase diagram.
- Reasoning
  - $\because$ Competition between thermal energy, intermolecular attraction, and structural order determines phase stability.
  - $\therefore$ Phase diagrams map where different microscopic organizations are thermodynamically favored.
- Takeaway
  - Phase behavior follows microscopic organization.

# Check Your Understanding

Using the water phase diagram:

(a) What happens to ice if pressure is increased at $-2\,^{\circ}\mathrm{C}$?

(b) Starting at $-30\,^{\circ}\mathrm{C}$ and $0.01\,\mathrm{kPa}$, what happens as temperature increases at constant pressure?

(c) Why do ice skates melt ice under the blade?

Come to lecture to see the answer.

# Part V

# Solids

# Outline of Part V: Solids

The Solid State of Matter

Lattice Structures in Crystalline Solids

# Outline of Part V: Solids

The Solid State of Matter

Lattice Structures in Crystalline Solids

# Crystalline vs. Amorphous Solids

## Crystalline Solids

Atoms, ions, or molecules arranged in a **regular, repeating pattern** (a lattice).

**Properties**:

- Sharp, precise melting point
- Anisotropic (properties vary by direction)

*Examples*: NaCl, diamond, ice, quartz, iron.

## Amorphous Solids

Particles arranged **randomly**, without long-range order.

**Properties**:

- Soften over a temperature *range* (no sharp MP)
- Isotropic (properties same in all directions)

*Examples*: glass, rubber, candle wax, many plastics.

Amorphous solids are sometimes described as **supercooled liquids** — their disordered structure is "frozen in" before crystallization can occur.

# Why Crystals Melt Sharply but Glasses Do Not

- Question
  - Why does one solid melt at one temperature while another softens gradually?
- Evidence
  - Crystals show a sharp melting temperature.
  - Amorphous solids soften across a temperature range.
- Reasoning
  - $\because$ Only crystals possess *long-range order* that can disappear collectively.
  - $\therefore$ Melting removes one ordered structure, but glasses only gain molecular mobility.
- Takeaway
  - Sharp transitions require collective structural order.

# Why Glasses Soften Instead of Melting

- Question
  - Why is the *glass transition* gradual rather than a true phase change?
- Evidence
  - Glasses retain disordered molecular arrangements after cooling.
  - Heating progressively lowers viscosity without latent heat.
- Reasoning
  - $\because$ Cooling trapped molecules before they reached equilibrium ordering.
  - $\therefore$ Heating restores motion continuously instead of destroying an ordered phase.
- Takeaway
  - Kinetic arrest produces gradual structural relaxation.

# Why Crystal Properties Depend on Direction

- Question
  - Why do crystals show direction-dependent properties while glasses do not?
- Evidence
  - Crystals cleave and transmit heat differently along different directions.
  - Glasses behave nearly identically in every direction.
- Reasoning
  - $\because$ Periodic atomic arrangements create preferred *crystallographic axes* for interactions.
  - $\therefore$ Ordered symmetry produces anisotropy, whereas random structures average directions equally.
- Takeaway
  - Atomic symmetry determines macroscopic directional behavior.

# Types of Crystalline Solids

| **Type** | **Particles** | **Bonding** | **Properties** |
|---|---|---|---|
| Ionic | cations & anions | electrostatic | Hard, brittle; high MP; nonconductor as a solid |
| Metallic | metal atoms + "sea" of $e^-$ | metallic | Malleable, ductile; good conductor; variable MP |
| Covalent network | atoms | covalent bonds throughout | Very hard; very high MP; usually nonconductor |
| Molecular | molecules | IMFs | Soft; low MP; nonconductor |

# Ionic Solids

- Composed of **cations** and **anions** held together by **electrostatic (ionic) attraction**.
- Typically **hard** and **brittle** — shifting layers brings like charges together ⇒ repulsion ⇒ shattering.
- **High melting points** (NaCl: 801 °C; MgO: 2852 °C).
- **Non-conductive** as solid (ions fixed in place); **conductive** when molten or dissolved.

## Examples

NaCl (table salt), KBr, NiO, $Al_2O_3$ (corundum/sapphire/ruby)

Higher ion charges ⇒ stronger attractions ⇒ higher MP.
MgO ($2^+$ / $2^-$) melts at 2852 °C; NaCl ($1^+$ / $1^-$) melts at 801 °C.

# Metallic Solids

- Composed of **metal atoms** surrounded by a delocalized "**sea of electrons**".
- Electrons flow freely ⇒ **excellent electrical and thermal conductors**.
- Layers of atoms slide past each other ⇒ **malleable** and **ductile**.
- **Metallic luster** due to interaction of light with free electrons.
- Melting points range widely: Hg (−39 °C) to W (3422 °C).

## Examples

Cu, Al, Fe, Au, Na, W, Hg

Alloys are metallic solids made of two or more metals (e.g. bronze = Cu + Sn; steel = Fe + C). They often have superior properties to the pure metals.

# Covalent Network Solids

- Atoms are connected by a **continuous network of covalent bonds** in 2D or 3D.
- Extremely **hard** and **high-melting** (covalent bonds must be broken throughout).
- Usually **non-conductive** (no free electrons or ions).

## Diamond

Each C atom is tetrahedrally bonded to 4 others in 3D.
MP $> 3500\,^{\circ}\mathrm{C}$. Hardest natural substance.

## Graphite (Exception)

C atoms form 2D layers; layers held by weak London forces.
**Soft** (layers slide) and **conductive** (delocalized $\pi$ electrons within layers).

Other examples: $SiO_2$ (quartz/sand), SiC (carborundum), Si (semiconductors).

# Molecular Solids

- Composed of **neutral molecules** held by **IMFs** (London forces, dipole-dipole, H-bonds).
- **Soft** and **low-melting**: IMFs are weak compared to ionic or covalent bonds.
- **Non-conductive** (no free charges).
- Melting point increases with stronger IMFs.

| **Substance** | **MP (°C)** | **Dominant IMF** |
|---|---|---|
| $H_2$ | $-259$ | London (nonpolar, tiny) |
| $CO_2$ | $-78.5$ (sublimes) | London (nonpolar) |
| $I_2$ | 114 | London (nonpolar, large) |
| $H_2O$ (ice) | 0 | Hydrogen bonding |
| Table sugar | 185 | H-bonding + London |

# Bonding Determines Solid Properties

- Question
  - Why do crystalline solids differ so greatly in melting point?
- Evidence
  - Molecular solids melt at very low temperatures.
  - Network solids melt only at extremely high temperatures.
- Reasoning
  - $\because$ Melting requires separating atoms from the attractive *pair potential*; stronger, more extensive bonding stores more energy.
  - $\therefore$ Network $>$ ionic $\approx$ metallic $>$ molecular in typical melting temperature.
- Takeaway
  - Bond energy predicts thermal stability.

# Bond Geometry Controls Mechanical Behavior

- Question
  - Why are ionic solids brittle but metals ductile?
- Evidence
  - Ionic crystals fracture when layers shift.
  - Metals deform permanently without shattering.
- Reasoning
  - $\because$ Ionic bonding requires specific charge alignment, whereas *delocalized electrons* maintain attraction during atomic rearrangement.
  - $\therefore$ Layer motion breaks ionic crystals but preserves metallic cohesion.
- Takeaway
  - Bond directionality governs mechanical response.

# Graphite Reveals Structure Matters

- Question
  - Why is graphite both electrically conducting and mechanically soft?
- Evidence
  - Graphite conducts within sheets.
  - Layers slide apart easily.
- Reasoning
  - $\because$ Covalent sheets contain *delocalized electrons*, while adjacent sheets interact mainly through weak dispersion forces.
  - $\therefore$ One structure produces both conductivity and softness.
- Takeaway
  - Structure modifies bonding predictions.

# Bonding Forms a Continuum

- Question
  - Why do some solids resist simple bonding classifications?
- Evidence
  - Semiconductors show partial charge transfer and finite electrical conductivity.
  - Bond polarity varies continuously among compounds.
- Reasoning
  - $\because$ Electron sharing changes continuously with atomic energy differences rather than by distinct categories.
  - $\therefore$ Measurements such as *band gap* reveal bonding character quantitatively.
- Takeaway
  - Bonding character is continuous, not categorical.

# Check Your Understanding

Classify each solid and predict whether it has a high or low melting point:

(a) Silicon dioxide ($SiO_2$, quartz)

(b) Ibuprofen ($C_{13}H_{18}O_2$, a drug molecule)

(c) Potassium iodide (KI)

(d) Copper (Cu)

Come to lecture to see the answer.

# Outline of Part V: Solids

The Solid State of Matter

Lattice Structures in Crystalline Solids

# Unit Cells

## Definition

A **unit cell** is the smallest repeating unit of a crystal lattice. Stacking unit cells in three dimensions reproduces the entire crystal.

Think of it like a single tile that, when repeated, tiles an infinite floor.

The unit cell is defined by:

- Three **edge lengths** ($a$, $b$, $c$)
- Three **angles** ($\alpha$, $\beta$, $\gamma$) between edges

For **cubic** unit cells, $a = b = c$ and $\alpha = \beta = \gamma = 90°$.
Three types of cubic cells: **simple cubic**, **body-centered cubic**, **face-centered cubic**.

# Why Describe Crystals with a Unit Cell?

- Question
  - Why can one small region describe an entire crystal?
- Evidence
  - X-ray diffraction repeats a regular pattern across macroscopic crystals.
  - Atomic neighborhoods recur throughout crystalline samples.
- Reasoning
  - $\because$ Repeating atomic arrangements remain unchanged after specific translations.
  - $\therefore$ One *unit cell* plus translation vectors reconstructs every atomic position and property.
- Takeaway
  - Translational symmetry compresses complete structural information.

# Why Are Only Certain Periodic Patterns Possible?

- Question
  - Why can only limited repeating geometries fill three-dimensional space?
- Evidence
  - Periodic crystals tile space without gaps or overlaps.
  - Fivefold rotations leave unavoidable gaps during repetition.
- Reasoning
  - $\because$ Every translation must reproduce identical neighboring environments everywhere.
  - $\therefore$ Only 14 *Bravais lattices* satisfy periodic tiling and symmetry simultaneously.
- Takeaway
  - Geometry constrains all periodic crystal structures.

# Why Begin with Cubic Crystal Structures?

- Question
  - Why does introductory chemistry emphasize cubic lattices?
- Evidence
  - Many metals, salts, and semiconductors crystallize in cubic forms.
  - Cubic cells have equal edges and right angles.
- Reasoning
  - $\because$ High symmetry makes atomic relationships predictable with minimal geometric complexity.
  - $\therefore$ Cubic lattices reveal *translational symmetry* while supporting later counting, density, packing, and diffraction.
- Takeaway
  - Simple symmetry exposes general crystal principles.

# Cubic Unit Cells

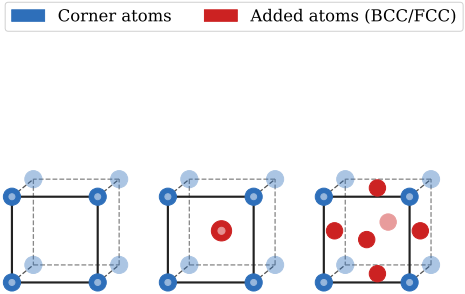
| | SC | BCC | FCC |
|---|---|---|---|
| Atoms in cell | 1 | 2 | 4 |
| Coord. number | 6 | 8 | 12 |
| Packing | 52% | 68% | 74% |

## Examples

- SC: Polonium (only element)
- BCC: Fe, Cr, Mo, W, K, Ba
- FCC: Al, Cu, Ag, Au, Ni, Pb

The **coordination number** is the number of nearest neighbors each atom touches.

Cubic Unit Cells



# Atom Counting in Unit Cells

## Fraction of Atom Belonging to a Unit Cell

- **Corner atom**: shared by 8 unit cells $\Rightarrow \frac{1}{8}$ per cell
- **Face atom**: shared by 2 unit cells $\Rightarrow \frac{1}{2}$ per cell
- **Edge atom**: shared by 4 unit cells $\Rightarrow \frac{1}{4}$ per cell
- **Body-center atom**: inside 1 cell $\Rightarrow$ 1 per cell

## Atom Count Verification

- SC: $8 \times \frac{1}{8} = \mathbf{1}$ atom/cell
- BCC: $8 \times \frac{1}{8} + 1 = \mathbf{2}$ atoms/cell
- FCC: $8 \times \frac{1}{8} + 6 \times \frac{1}{2} = \mathbf{4}$ atoms/cell

# Example: Density from Unit Cell

## Density of Aluminum — (chem2e ch10)

Aluminum forms an FCC unit cell with an edge length of 404.95 pm. Calculate the density of aluminum.
(MW of Al: $26.98\,\frac{\text{g}}{\text{mol}}$; $N_A = 6.022 \times 10^{23}\,\frac{1}{\text{mol}}$)

FCC: 4 atoms/unit cell.

$$m_{\text{cell}} = \frac{4\,\text{atoms}}{\text{cell}} \times \frac{26.98\,\text{g}}{6.022 \times 10^{23}\,\text{atoms}}$$

$$m_{\text{cell}} = 1.792 \times 10^{-22}\,\text{g}$$

$$a = 404.95\,\text{pm} = 4.0495 \times 10^{-8}\,\text{cm}$$

$$V_{\text{cell}} = a^3 = 6.647 \times 10^{-23}\,\text{cm}^3$$

$$\boxed{d = \frac{m}{V} = \frac{1.792 \times 10^{-22}\,\text{g}}{6.647 \times 10^{-23}\,\text{cm}^3} = 2.697\,\frac{\text{g}}{\text{cm}^3}}$$

Literature value for Al:
$2.699\,\frac{\text{g}}{\text{cm}^3}$

Excellent agreement — unit cell geometry encodes bulk density!

# Check Your Understanding

Iron (Fe) forms a BCC unit cell with an edge length of 287 pm.

(a) How many Fe atoms are in one unit cell?

(b) Is the coordination number 6, 8, or 12?

(c) Without calculating, predict whether Fe's density will be greater or less than Al's ($2.70\,\frac{\text{g}}{\text{cm}^3}$). Why?

Come to lecture to see the answer.

# Why Must Boundary Atoms Be Shared?

- Question
  - Why do corner, edge, and face atoms contribute only fractions?
- Evidence
  - Neighboring unit cells contain the same boundary atoms.
  - Large crystals satisfy total atoms = cells $\times$ atoms per cell.
- Reasoning
  - $\because$ Boundary atoms physically belong to every adjacent cell simultaneously.
  - $\therefore$ Equal sharing uniquely prevents overcounting as crystal size increases.
- Takeaway
  - Sharing preserves consistent atom counting.

# Why Is Twelve the Maximum Coordination Number?

- Question
  - Why can one atom touch at most twelve equal neighbors?
- Evidence
  - FCC crystals give every atom 12 nearest neighbors.
  - A thirteenth equal sphere cannot touch without overlap.
- Reasoning
  - $\because$ Twelve neighbors already occupy every available direction around the central atom.
  - $\therefore$ Additional contact requires overlapping electron clouds, which atoms resist.
- Takeaway
  - Geometry limits nearest-neighbor contacts.

# Why Do Coordination and Packing Efficiency Track Together?

- Question
  - Why do FCC and HCP share coordination and packing despite different unit cells?
- Evidence
  - FCC and HCP both have coordination number 12.
  - Both occupy 74% of space with equal spheres.
- Reasoning
  - $\because$ Local neighbor geometry determines how efficiently equal spheres fill nearby space.
  - $\therefore$ Packing efficiency follows coordination; stacking sequence changes the unit cell, not local contacts.
- Takeaway
  - Local geometry governs bulk packing.

# Packing Efficiency

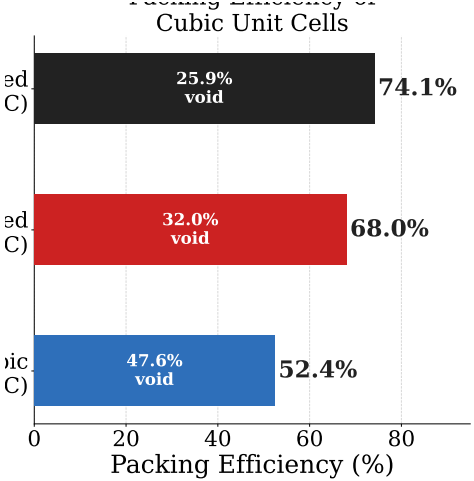
## Definition

**Packing efficiency** = fraction of unit cell volume occupied by atoms.

## Calculated Values

- **Simple cubic**: 52% (least efficient; only Po)
- **Body-centered cubic**: 68% (common for metals)
- **Face-centered cubic**: 74% (most efficient; = hexagonal closest packing)

FCC/HCP are the most efficient ways to pack spheres of equal size. The remaining 26% is empty space (interstitial space).



# Why Does FCC Reach the Greatest Packing Efficiency?

- Question
  - Why does FCC occupy more space than BCC or SC?
- Evidence
  - FCC spheres touch along each face diagonal.
  - BCC spheres touch only along each body diagonal.
- Reasoning
  - $\because$ Face-diagonal contact lets equal spheres approach without overlap before the unit cell expands.
  - $\therefore$ FCC fills 74.05%, whereas BCC reaches only 68%.
- Takeaway
  - Contact geometry determines maximum packing.

# Why Do Atoms Prefer Close-Packed Structures?

- Question
  - Why does nature often favor densely packed lattices?
- Evidence
  - Most elemental metals crystallize as FCC or HCP.
  - Both structures give each atom 12 nearest neighbors.
- Reasoning
  - $\because$ More neighbors at equilibrium spacing create more stabilizing attractive interactions without stronger overlap.
  - $\therefore$ Close packing usually minimizes crystal potential energy.
- Takeaway
  - Stable lattices maximize favorable neighbor interactions.

# Why Can Polonium Adopt Simple Cubic Packing?

- Question
  - Why does polonium remain stable despite inefficient packing?
- Evidence
  - Polonium crystallizes in the simple cubic structure.
  - Simple cubic has coordination number 6 and 52% packing.
- Reasoning
  - $\because$ Relativistic electronic effects alter bonding directions and outweigh purely geometric packing preferences.
  - $\therefore$ Electronic structure can stabilize less densely packed lattices.
- Takeaway
  - Bonding energy ultimately selects crystal structure.

# Ionic Crystal Structures

Ionic crystals arrange cations into the **holes** of the anion lattice (or vice versa). The type of hole depends on the **cation-to-anion radius ratio**.

| **Structure** | **Ratio** | **CN** | **Example** |
|---|---|---|---|
| NaCl (rock salt) | FCC anions; cations in octahedral holes | 6:6 | NaCl, KBr, MgO |
| CsCl | SC anions; cation in cubic hole | 8:8 | CsCl |
| ZnS (zinc blende) | FCC anions; cations in ½ tetrahedral holes | 4:4 | ZnS, GaAs |
| $CaF_2$ (fluorite) | FCC $Ca^{2+}$; $F^-$ in all tetrahedral holes | 8:4 | $CaF_2$, $UO_2$ |

# X-Ray Diffraction and Bragg's Law

## How Crystal Structures Are Determined

X-rays are diffracted by the regularly spaced planes of atoms in a crystal. Constructive interference occurs only when Bragg's condition is met:

$$n\lambda = 2d\sin\theta$$

- $n$ = order of diffraction (integer)
- $\lambda$ = X-ray wavelength
- $d$ = spacing between crystal planes
- $\theta$ = diffraction ("glancing") angle

## Example

X-rays ($\lambda = 154\,\text{pm}$) diffract at $\theta = 14.2°$ from a crystal plane.
First-order ($n = 1$):

$$d = \frac{n\lambda}{2\sin\theta} = \frac{1 \times 154\,\text{pm}}{2\sin(14.2°)} = \boxed{314\,\text{pm}}$$

# Why Does Bragg's Law Predict Diffraction Peaks?

- Question
  - Why do only certain X-ray angles produce strong reflected intensity?
- Evidence
  - Adjacent lattice planes are separated by distance $d$.
  - The lower ray travels an extra distance entering and leaving the crystal.
- Reasoning
  - $\because$ The extra path equals $2d\sin\theta$; both travel segments contribute equally.
  - $\therefore$ Constructive interference occurs only when $2d\sin\theta = n\lambda$.
- Takeaway
  - Diffraction measures periodic atomic spacing.

# Why Must X-Rays Match Atomic Dimensions?

- Question
  - Why can X-rays reveal atoms while visible light cannot?
- Evidence
  - Atomic plane spacings are about 100 pm.
  - Visible wavelengths are thousands of times larger.
- Reasoning
  - $\because$ Significant path differences require wavelengths comparable to plane spacing.
  - $\therefore$ Visible waves barely distinguish adjacent planes, but X-rays diffract strongly.
- Takeaway
  - Resolution requires wavelength matching structure size.

# Why Does One Crystal Produce Many Diffraction Peaks?

- Question
  - Why does one crystal generate many distinct Bragg reflections?
- Evidence
  - A crystal contains many parallel plane families.
  - Each *Miller index* (*hkl*) identifies one plane spacing.
- Reasoning
  - $\because$ Different plane families have different spacings, creating different path differences.
  - $\therefore$ Each allowed spacing produces its own diffraction peak.
- Takeaway
  - Diffraction maps three-dimensional crystal geometry.

# Check Your Understanding

A sodium chloride (NaCl) crystal is irradiated with X-rays of wavelength 154 pm.

The first-order diffraction peak appears at $\theta = 13.7°$.

What is the spacing $d$ between crystal planes?

Come to lecture to see the answer.

# Summary: Chapter 10

- **IMFs** (London, dipole-dipole, H-bonding, ion-dipole) determine physical properties of liquids and solids.
- **Surface tension**, **viscosity**, and **capillary action** arise from the interplay of cohesive and adhesive forces.
- **Vapor pressure** increases with temperature; the Clausius-Clapeyron equation quantifies this: $\ln(P_2/P_1) = (\Delta H_{\text{vap}}/R)(1/T_1 - 1/T_2)$.
- **Heating curves** show temperature vs. heat added; plateaus occur during phase transitions.
- **Phase diagrams** map stable phases vs. P and T; triple points and critical points define special states.
- Crystalline solids are classified as **ionic, metallic, covalent network**, or **molecular** based on their bonding.
- **Cubic unit cells** (SC, BCC, FCC) are characterized by atoms/cell, coordination number, and packing efficiency; density can be calculated from unit cell dimensions.
- **Bragg's Law** ($n\lambda = 2d\sin\theta$) relates X-ray diffraction angles to crystal plane spacing.