- → Because this effect arises from attractions between *pairs* of molecules, it should be proportional to the *square* of the number of molecules per unit volume $(N/V)^2$, or equivalently, to the *square* of the molar concentration $(n/V)^2$.
- → The pressure is predicted to be reduced by an amount $a(n/V)^2$, where a is a positive constant that depends on the strength of the attractive forces.
- → The potential energy describing this situation is that of long-range attraction with the form $-(1/r^6)$, where r is the distance between a pair of gas-phase molecules. This type of attraction primarily arises from *dispersion* or *London* forces (see **Topic 3F.4**).
- → The units of a are $L^2 \cdot atm \cdot mol^{-2}$.

Summary

- **Virial equation**
  - → Describes real gases
- **Van der Waal's equation**
  - → An *approximate* equation of state
  - → Takes molecular volume and intermolecular forces into account
- **Ideal gas equation**
  - → Least accurate of the gas-phase equations of state
  - → Ignores molecular volume and intermolecular forces
  - → Easiest to use

3E.3 The Liquefaction of Gases

- **Joule–Thomson effect**
  - → When attractive forces dominate, a real gas *cools* as it expands.
  - → In this case expansion requires energy that comes from the kinetic energy of the gas, lowering the temperature. (The gas to be liquefied is compressed and then allowed to expand through a small hole.) Exceptions are He and H_2, for which repulsion dominates.
  - → Expansion cooling is used in some refrigerators and to effect the condensation of gases such as oxygen, nitrogen, and argon.

Topic 3F: INTERMOLECULAR FORCES

3F.1 The Origin of Intermolecular Forces

- **Physical states**
  - → Solid, liquid, and gas

- **Phase**
  - → Form of matter uniform in both chemical composition and physical state (solid, liquid, or gas)
  - → See **Table 3F.2** for melting and boiling points of substances.
- **Condensed phase**
  - → Solid or liquid phase
    Examples: Ag(s); Sn/Pb(s) alloy, composition variable; $H_2O(s)$; $H_2O(l)$; 1% NaCl(s) in $H_2O(l)$
  - → Molecules (or atoms or ions) are close to each other all the time, and intermolecular forces are of major importance.
- **Coulomb potential energy E_P**
  - → The interaction between two charges, Q_1 and Q_2, separated by distance r is ⇒

$$\boxed{E_P \propto \frac{Q_1 Q_2}{r}}$$

  - → See **Topic 1D.1** and **Fundamentals Topic A.**
  - → Almost all intermolecular interactions can be traced back to this fundamental expression.

Note: The term *intermolecular* is used in a general way to include atoms and ions.

3F.2 Ion-Dipole Forces

- **Hydration**
  - → Attachment of water molecules to ions (cations and anions)
  - → Water molecules are polar and have an electric dipole moment $\mu(H_2O)$.
  - → A small positive charge on each H atom attracts anions, and a small negative charge on the O atom attracts cations.
- **Ion-dipole interaction**
  - → The potential energy (interaction) between an ion with charge $|z|$ and a polar molecule with dipole moment μ at a distance r is ⇒

$$\boxed{E_P \propto -\frac{|z|\mu}{r^2}}$$

  - → For proper *alignment* of the ion and dipole, the interaction is *attractive*: Cations attract the *partial* negative charges, and anions attract the *partial* positive charges on the polar molecule.
  - → Shorter range (r^{-2}) interaction than the Coulomb potential (r^{-1})
  - → Polar molecule needs to be *almost* in contact with ion for substantial ion-dipole interaction.
- **Hydrated compounds**
  - → Ion-dipole interactions are much *weaker* than ion-ion interaction but are relatively strong for *small, highly charged* cations (large $|z|$, small r).
  - → Accounts for the formation of salt hydrates such as $CuSO_4 \cdot 5\,H_2O$ and $CrCl_3 \cdot 6\,H_2O$
- **Size effects**
  - → Li^+ and Na^+ (small) tend to form hydrated compounds.
  - → K^+, Rb^+, and Cs^+ (larger) tend not to form hydrates.

  - Effective radius of NH_4^+ (143 pm) is similar in radius to Rb^+ (149 pm). NH_4^+ forms *anhydrous* compounds.
- **Charge effects**
  - Ba^{2+} and K^+ are similar in size, yet Ba^{2+} (larger charge) forms *hydrates*.

3F.3 Dipole-Dipole Forces

- **Dipole alignment**
  - In solids, molecules with dipole moments tend to *align* with partial positive charge on one molecule near the partial negative charge on another.
- **Dipole-dipole interaction in solids**
  - The interaction between two polar molecules with dipole moments μ_1 and μ_2 *aligned* and separated by a distance r is ⇒

$$\boxed{E_P \propto -\frac{\mu_1 \mu_2}{r^3}}$$

  - *Attractive* interaction in solids for head-to-tail *alignment* of dipoles
  - Shorter range (r^{-3}) interaction than ion-dipole (r^{-2}) or Coulomb potential (r^{-1})
  - For significant interaction, polar molecules must be *almost* in contact with each other.
- **Dipole-dipole interactions in gas-phase molecules**
  - Dipole-dipole interactions are much *weaker* in gases than in solids. The potential energy of interaction is ⇒

$$\boxed{E_P \propto -\frac{\mu_1^2 \mu_2^2}{r^6}}$$

  - Because gas molecules are in motion (rotating as well), they are subject to only a *weak* net attraction because of *occasional* alignment.
- **Dipole-dipole interactions in liquid-phase molecules**
  - Same potential energy relationship as in the gas phase, but the interaction is somewhat *stronger* because the molecules are closer.
  - The liquid *boiling point* is a measure of the *strength* of the intermolecular forces in a liquid. The boiling point of isomers is *often* related to the strength of their dipole-dipole interactions.
  - Typically, the *larger* the dipole moment, the *higher* the boiling point (often a relatively small effect).

    Example: *cis*-dibromoethene (dipole moment ≈ 2.4 D, bp 112.5 °C) versus *trans*-dibromoethene (zero dipole moment, bp 108 °C)

3F.4 London Forces

- **Nonpolar molecules**
  - Condensation of *nonpolar* molecules to form liquids implies the existence of a type of intermolecular interaction other than those described earlier.
- **London force**
  - Occurs in addition to any dipole-dipole interactions
  - Is universal; applies to all molecules

  - Accounts for the attraction between any pair of ground-state molecules (*polar* or *nonpolar*)
  - Arises from *instantaneous* partial charges (*instantaneous* dipole moment) in one molecule *inducing* partial charges (dipole moment) in a neighboring one
  - Exists between atoms and *rotating* molecules as well
  - Strength depends on polarizability and shape of molecule.

    Example: Other things equal, rod-shaped molecules tend to have stronger London forces than spherical molecules because they can approach each other more closely.
- **Polarizability, α**
  - Of a molecule is related to the ease of deformation of its electron cloud
  - Is proportional to the total number of electrons in the molecule
  - Because the number of electrons correlates with molar mass (generally increases), polarizability does as well.
  - The potential energy between two molecules (polar or nonpolar) with polarizability α_1 and α_2, separated by a distance r, is ⇒

$$\boxed{E_P \propto -\frac{\alpha_1 \alpha_2}{r^6}}$$

    Note: Same (r^{-6}) dependence as dipole-dipole (r^{-6}) with *rotating* molecules, but the London interaction is *usually* stronger at normal temperatures.
- **Liquid boiling point**
  - A measure of the strength of intermolecular forces in a liquid
  - In comparing the interactions discussed in **Topics 3F.3** and **3F.4**, the *major* influence on boiling point in both *polar* and *nonpolar* molecules is the London force.

    Example: We can predict the relative boiling points of the nonpolar molecules: F_2, Cl_2, Br_2, and I_2. Boiling point correlates with polarizability, which depends on the number of electrons in the molecule. The boiling points are expected to increase in the order of F_2 (18 electrons), Cl_2 (34), Br_2 (70), and I_2 (106). The experimental boiling temperatures are F_2 (−188 °C), Cl_2 (−34 °C), Br_2 (59 °C), and I_2 (184 °C).
- **Dipole-induced dipole interaction**
  - The potential energy between a polar molecule with dipole moment μ_1 and a nonpolar molecule with polarizability α_2 at a distance r is ⇒

$$\boxed{E_P \propto -\frac{\mu_1^2 \alpha_2}{r^6}}$$

  - Also applies to molecules that are both polar: each one can induce a dipole in the other.
  - Weaker interaction than dipole-dipole

    Example: Carbon dioxide ($\mu = 0$) dissolved in water ($\mu > 0$)

3F.5 Hydrogen Bonding

- **Hydrogen bonds**
  - Interaction *specific* to certain types of molecules (with strong attractive forces)
  - Account for unusually high boiling points in ammonia (NH_3, −33 °C), water (H_2O, 100 °C), and hydrogen fluoride (HF, 20 °C)

→ Arise from an H atom, *covalently* bonded to a N, O, or F atom in *one* molecule, strongly attracted to a *lone pair* of electrons on a N, O, or F atom in *another* molecule

→ Are *strongest* when the three atoms are in a *straight line* and the distance between terminal atoms is within a given range

→ Common symbol for the H bond is three dots: ···

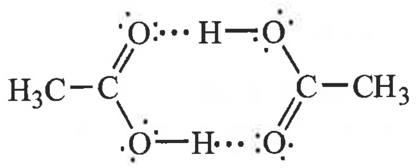
→ *Strongest* intermolecular interaction between *neutral* molecules

Examples: N–H··· :N hydrogen bonds between NH_3 molecules in pure NH_3
O–H··· :O hydrogen bonds between H_2O molecules in pure H_2O

- **Hydrogen bonding in gas-phase molecules**

  → Aggregation of some molecules persists in the vapor phase.

  → In HF, fragments of *zigzag* chains and $(HF)_6$ rings are formed. In CH_3COOH (acetic acid), hydrogen-bonded *dimers* are formed. The abbreviated (no C–H bonds shown) Lewis structure of the dimer $(CH_3COOH)_2$ is shown on the right.



- **Importance of hydrogen bonding**

  → Accounts for the open structure of solid water

  → Maintains the shape of biological molecules

  → Binds the two strands of DNA together

3F.6 Repulsions

- **Nature of repulsions**

  → Molecules (or atoms that do not form bonds) that are very close together repel one another.

  → The Pauli exclusion principle forms the basis of understanding this repulsion.

Example: As two He atoms approach each other, at short separations, their 1*s* atomic orbitals overlap and form a bonding and an antibonding molecular orbital.

The bonding molecular orbital is filled with two electrons, and the remaining two electrons are required by the exclusion principle to fill the antibonding orbital.

An antibonding orbital is more antibonding in character than a bonding orbital is bonding; the result is an increase in energy as the two atoms merge into each other.

The same effect occurs for all molecules whose atoms have filled shells (e.g., H_2), even though the details of the bonding and antibonding orbitals they form may be much more complicated.

The result is that all molecules repel each other when they come into contact and their orbitals overlap.

- **Electron density**

  → Electron density in all atomic orbitals (AOs) and the molecular orbitals (MOs) they form decreases exponentially toward zero at large distances from the nucleus.

  → The overlap between orbitals on neighboring molecules will also depend exponentially on their separation.

  → As a result, repulsions between molecules usually depend exponentially on separation (see text **Figure 3F.1**). Repulsions are effective only when the two molecules are very close together. Once they are close, the energy of repulsion increases rapidly as the distance between the two molecules decreases.

  → The strong dependence of repulsion on separation is the underlying reason objects around us have definite, well-defined shapes.

Topic 3G: LIQUIDS

3G.1 Order in Liquids

- **Liquid phase**

  → Mobile molecules with restricted motion

  → Between the extremes of gas and solid phases

- **Long-range order**

  → Characteristic of a *crystalline solid*

  → Atoms or molecules are arranged in orderly patterns that are repeated over long distances.

- **Short-range order**

  → Characteristic of the *liquid phase*

  → Atoms or molecules are positioned in orderly patterns at nearest-neighbor distances only.

  → Local order is maintained by a continual process of forming and breaking nearest-neighbor interactions.

3G.2 Viscosity and Surface Tension

- **Viscosity**

  → Resistance of a substance to flow: *Greater* viscosity yields *slower* flow.

  → Viscous liquids include those with hydrogen bonding between molecules.

Examples of liquids with high viscosity:

H_3PO_4 (phosphoric acid) and $C_3H_8O_3$ (glycerol) (each forms many H bonds); liquid phases of metals; and long-chain molecules that can be entangled, such as hydrocarbon oil and greases

- **Viscosity and temperature**
  - → *Usually* viscosity *decreases* with *increasing T*

    Exception: Unusual behavior of sulfur, for which viscosity initially increases with increasing *T* as S_8 rings break, forming chains that tangle together
- **Surface tension (several definitions)**
  - → Tendency of surface molecules in a liquid to be pulled into the interior of the liquid by an imbalance in intermolecular forces
  - → *Inward pull* that determines the resistance of a liquid to an increase in surface area
  - → A measure of the *force* that must be applied to *surface molecules* so that they undergo the same *force* as molecules in the *interior* of the liquid
  - → A measure of the tightness of the surface layer (Symbol: γ (gamma) Units: $N{\cdot}m^{-1}$ or $J{\cdot}m^{-2}$)
- **Capillary action**
  - → Rise of liquids up narrow tubes when the *adhesion* forces are greater than *cohesion* forces
  - → **adhesion:** Forces that bind a *substance* to a *surface*
  - → **cohesion:** Forces that bind *molecules* of a substance together to form a *bulk material*
- **Meniscus (curved surface that a liquid forms in a tube)**
  - → *Adhesive* forces greater than *cohesive* forces (forms a ∪ shape)
  - → *Cohesive* forces greater than *adhesive* forces (forms a ∩ shape)
  - → Glass surfaces have exposed O atoms and O–H groups to which hydrogen-bonded liquids such as H_2O can bind. In this case, the *adhesive* forces are greater than the *cohesive* ones. Water *wets* glass, forms a ∪ shape at the surface, and undergoes a capillary rise in a glass tube.
  - → Mercury liquid does not bind to glass surfaces. The *cohesive* forces are greater than the *adhesive* ones. Mercury does *not* wet glass, forms a ∩ shape at the surface, and undergoes a capillary *lowering* in a glass tube.

3G.3 Liquid Crystals

- → Materials that cannot be characterized as solid, liquid, or gas
- → Substances that flow like viscous liquids but whose molecules form a moderately ordered array similar to that in a crystal.
- → Examples of a *mesophase,* an intermediate state of matter with the fluid properties of a liquid and some molecular ordering similar to that of a crystal

- **Isotropic material**
  - → Properties independent of the direction of measurement

    Ordinary liquids are isotropic, with viscosity values equal in every direction.
- **Anisotropic material**
  - → Properties depend on the direction of measurement

Certain rod-shaped molecules form liquid crystals, in which molecules are free to slide past one another along their axes but resist motion perpendicular to that direction.

- **Classes of liquid crystals**
  - → Differ in the arrangement of the molecules

    See text **Figures 3G.7**, **3G.8**, and **3G.9**.

Nematic phase: Molecules lie together in the same direction but are *staggered.*

Smectic phase: Molecules lie together in the same direction in *layers*, but not staggered.

Cholesteric phase: Molecules form *nematiclike layers*, but the molecules of neighboring layers are *rotated* with respect to each other. The resulting liquid crystal has a *helical* arrangement of molecules.

- **Thermotropic liquid crystals**
  - → Made by melting solid-phase material
  - → Exist over small temperature range between solid and liquid

    Example: *p*-azoxyanisole
- **Lyotropic liquid crystals**
  - → Layered structures produced by the action of a solvent on a solid or a liquid.
  - → Examples include cell membranes and aqueous solutions of detergents and lipids (fats).

3G.4 Ionic Liquids

- → Molecular substances tend to have low melting points.
- → Ionic, network, and metallic substances tend to have high melting points.
- → Ionic liquids are exceptions.
- → Ionic liquids are ionic substances with low melting points. They can be liquid at room temperature and below.
- → Ionic liquids have remarkably low vapor pressures; they constitute a new class of solvents developed to have low vapor pressures but also to dissolve organic compounds.
- → Compounds in which one of the ions (usually the cation) is a large, organic ion that prevents the liquid from crystallizing at ordinary temperatures

  Example: Cation: 1-Butyl-3-methylimidazolium (**Margin Figure 4** on **page 199** in the text)
  Anion: Tetrafluoroborate: BF_4^-
- → One formulation is used to dissolve rubber in old tires for recycling.
- → Another is used to extract radioactive waste from groundwater.

Topic 3H: SOLIDS

3H.1 Classification of Solids

- **Amorphous solid**
  - → Atoms or molecules (neutral or charged) lie in random positions.
- **Crystalline solid**
  - → Atoms, ions, or molecules are associated with points in a **lattice**, which is an *orderly* array of equivalent points in three dimensions.
  - → Structure has long-range order.
- **Crystal faces**
  - → Flat, well-defined planar surfaces with definite interplanar angles
- **Classification of crystalline solids**

Metallic solids:	Cations in a sea of electrons **Examples:** Fe(s), Li(s)
Ionic solids:	Mutual attractions of cations and anions **Examples:** NaCl(s), $Ca(SO_4)_2$(s)
Molecular solids:	Discrete molecules held together by the *intermolecular forces* discussed earlier **Examples:** sucrose, $C_{12}H_{22}O_{11}$(s); ice, H_2O(s); benzene(s)
Network solids:	Atoms bonded *covalently* to their neighbors throughout the entire solid **Examples:** diamond, C(d); graphite planes, C(gr)

3H.2 Molecular Solids

- → Solid structures that reflect the nonspherical nature of their molecules and the relatively weak intermolecular forces that hold them together
- → Characterized by low melting temperatures and less hardness than ionic solids
- → May be amorphous (wax) or crystalline (sucrose)

3H.3 Network Solids

- **Crystals**
  - → Atoms joined to neighbors by *strong* covalent bonds that form a network extending throughout the solid
  - → Characterized by high melting and boiling temperatures
  - → Tend to be hard and rigid structures (diamond)
- **Elemental network solids**
  - → Network solids formed from one element only, such as the allotropes graphite and diamond, in which the carbon atoms are connected differently
  - → *Allotropes* are forms of an element with different solid-state structures.

- **Graphite**
  - → The thermodynamically stable allotrope of carbon (Soot contains small crystals of graphite.)
  - → Produced pure commercially by heating C rods in an electric furnace for several days
  - → Contains sp^2-hybridized C atoms
  - → Consists structurally of large sheets of fused benzene-like hexagonal units. A π-bonding network of delocalized electrons accounts for the high electrical conductivity of graphite.
  - → When certain impurities are present, graphitic sheets can slip past one another, and graphite becomes an excellent dry lubricant.
  - → Graphite is soluble only in a few liquid metals.
  - → Soot and carbon black have commercial applications in rubber and inks. Activated charcoal is an important, versatile purifier. Unwanted compounds are adsorbed onto its microcrystalline surface.
  - → A chicken-wire-like sheet of carbon atoms in graphite is called a *graphene* sheet. Graphene, a single monolayer sheet of graphite, is a new material with exceptional promise in the electronics industry.
  - → Very pure sheets of graphene can be prepared and stacked together with water molecules that act as a kind of glue between them.
  - → The result is a very strong, flexible, but very thin paperlike material that conducts electricity but is tougher than diamond.
- **Diamond**
  - → Found naturally embedded in *kimberlite*, a soft rock
  - → Hardest substance known and an excellent conductor of heat
  - → An excellent abrasive, and the heat generated by friction is rapidly conducted away
  - → Natural diamonds are mined extensively. Synthetic diamonds are produced from graphite at high pressures (> 80 kbar) and temperatures (> 1500 °C) and by thermal decomposition of methane (the preferred method).
  - → Diamond is soluble in liquid metals, such as Cr and Fe, but less soluble than graphite. This solubility difference is utilized in synthesizing diamond at high pressure and high temperature.
  - → Carbon in diamond is sp^3-hybridized, and each C atom in a diamond crystal is bonded directly to four other C atoms and indirectly interconnected to all of the other C atoms in the crystal through C–C single σ-bonds.
  - → The σ-bonding network of localized electrons accounts for the electrical insulating properties of diamond.
- **Ceramics**
  - → Usually oxides with a network structure having great strength and stability because covalent bonds must break to deform the crystal
  - → Tend to shatter rather than bend under stress

    Examples: Quartz, silicates, and high-temperature superconductors

3H.4 Metallic Solids

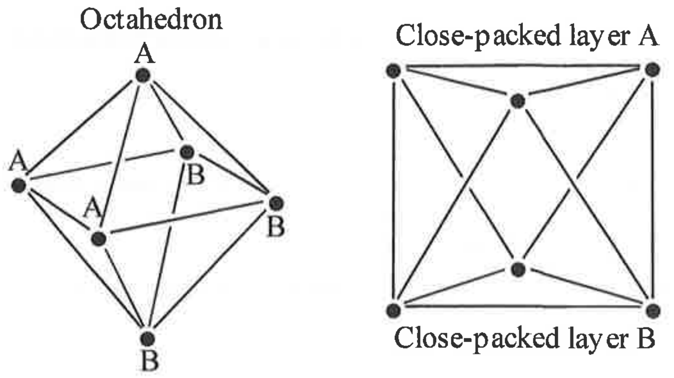
- **Close-packed structures**
  - → Atoms occupy smallest total *volume* with the *least* amount of empty space.
  - → Metal atoms are treated as *spheres* with radii *r*.
  - → Type of metal determines whether a close-packed structure is assumed.
- **Close-packed layer**
  - → Atoms (*spheres*) in a planar arrangement with the *least* amount of empty space; contour of the layer has *dips* or *depressions.*
  - → Each atom in a layer has *six* nearest neighbors (hexagonal pattern).
  - → Layers stack such that bottoms of spheres in one layer fit in *dips* of the layer below.
- **Stacked layers**
  - → In a close-packed structure, each atom has *three* nearest neighbors in the layer above, *six* in its original layer, and *three* in the layer below, for a total of 12 nearest neighbors.
- **Coordination number (CN)**
  - → Number of nearest neighbors of each atom in the solid
  - → Impossible to pack identical spheres (metal atoms) with CN > 12
- **Two arrangements of stacking close-packed layers**

Pattern:	ABABABAB...	hcp ≡ *hexagonal close-packing* (repeat after two layers)
	ABCABCABC...	ccp ≡ *cubic close-packing* (repeat after three layers)

- **Occupied space in hcp/ccp structures**
  - → 74% of space is occupied by the spheres and 26% is *empty*.
- **Tetrahedral hole**
  - → Formed when a *dip* between *three* atoms in one layer is *covered* by *another* atom in an adjacent layer
  - → Two tetrahedral holes per atom in a close-packed structure (hcp or ccp)
- **Octahedral hole**
  - → Space between *six* atoms, *four* of which are at the corners of a square plane, forms an octahedral hole. The square plane is oriented 45° with respect to two close-packed layers. *Two* atoms in the square plane are in layer **A** and the other *two* in layer **B**. There is *one* additional atom in layer **A** that is *above* the square plane and *another* in layer **B** that is *below* the square plane. The result is an octahedral arrangement of six atoms with a hole in the center.

  - → One octahedral hole per atom in a close-packed structure (hcp or ccp)

Figure of an octahedron and an octahedron rotated to show the relation to two close-packed layers



- **Body-centered cubic (bcc) structure**
  - → Coordination number of 8 (*not* close-packed)
  - → Spheres touch along the *body* diagonal of a cube.
  - → Can be converted into close-packed structures under high pressure
- **Primitive cubic (pc) structure**
  - → Coordination number of 6 (*not* close-packed)
  - → Spheres touch along the *edge* of the cube. Only one known example: Po (polonium)

Crystal Structure	Coordination Number	Occupied Space	Examples
ccp (fcc)	12	74%	Ca, Sr, Ni, Pd, Pt, Cu, Ag, Au, Al, Pb Group 18: noble gases at low *T*, except He
hcp	12	74%	Be, Mg, Ti, Co, Zn, Cd, Tl
bcc	8	68%	Group 1: alkali metals, Ba, Cr, Mo, W, Fe
pc	6	52%	Po (covalent character)

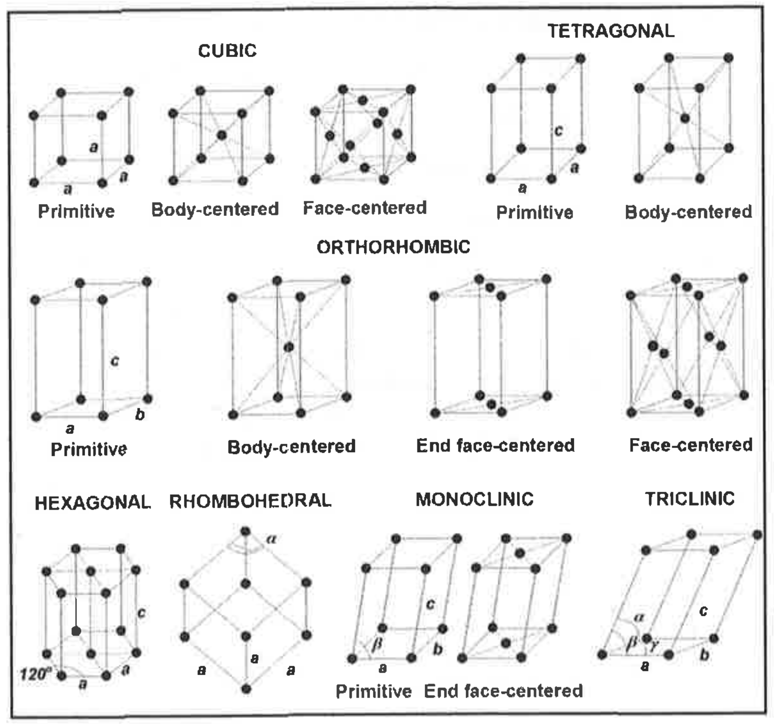
3H.5 Unit Cells

- **Lattice**
  - → A regular array of equivalent points in three dimensions (or any other dimensions)
- **Unit cell**
  - → Smallest repeating unit that generates the full array of points by translation
- **Crystal**
  - → Constructed by associating atoms, ions, or molecules with each lattice point

→ **Metallic crystals:** One metal atom per lattice point (ccp (fcc), bcc, pc)
Two metal atoms per lattice point (hcp)

- **Unit cells for metals**
  → Cubic system: pc, bcc, and fcc (ccp)
  → Hexagonal system: *primitive unit cell* with *two* atoms per lattice point (hcp)
- **Unit cells in three dimensions**
  → Edge lengths: a, b, c
  → Angles between two edges: α (between edges b and c); β (between a and c); γ (between a and b)
- **Seven crystal systems (unit cell shapes)**
  → Cubic, hexagonal, tetragonal, orthorhombic, rhombohedral, monoclinic, and triclinic
- **Bravais lattices**
  → 14 basic patterns of arranging points in three dimensions
  → Each pattern has a different unit cell (figure).

The 14 Bravais Lattices ⇒



- **Volume of several types of unit cells**
  Cubic: $V = a \times a \times a = a^3$
  $(\alpha = \beta = \gamma = 90°)$
  Tetragonal: $V = a \times a \times c = a^2c$
  $(\alpha = \beta = \gamma = 90°)$
  Orthorhombic: $V = a \times b \times c = abc$
  $(\alpha = \beta = \gamma = 90°)$
- **Properties of unit cells**
  → Each *corner point* shared among 8 cells (1/8 per cell)
  8 corner points × 1/8 per cell = 1 corner point per cell (*all cells*)
  → Each *face-centered point* shared between 2 cells (1/2 per cell)
  6 face points × 1/2 per cell = 3 face points per cell (*face-centered cells*)
  2 face points × 1/2 per cell = 1 face point per cell (*end face-centered cells*)
  → Each *body-centered point* unshared (1 per cell)
  1 body point × 1 per cell = 1 body point per cell (*body-centered cells*)

- **Properties of *cubic system* unit cells**
  → *One* metal atom occupies each *lattice point*

Primitive

One metal atom (*sphere*) at each *corner point* in a unit cell
(*one* atom (radius r) per cell)
Spheres *touch* along an *edge:* $a = 2r$
Volume of the unit cell: $V = a^3 = (2r)^3 = 8r^3$
Density of a pc metal: (M = molar mass):

$$\boxed{d = \frac{(\text{1 atom per cell})(\text{mass of one atom})}{(\text{volume of one unit cell})} = \frac{M/N_\text{A}}{a^3} = \frac{M/N_\text{A}}{8r^3}}$$

Body-centered

One metal atom (*sphere*) at each *corner point* in a unit cell
One metal atom (*sphere*) at the *center* of the unit cell
Total atoms in unit cell = 8 (1/8) + 1 (1) = 2
(*two* atoms (radius r) per unit cell (edge length a))
Spheres *touch* along the *body diagonal:* $\sqrt{3}a = 4r$ or $a = \frac{4}{\sqrt{3}}r$
Volume of the unit cell: $V = a^3 = \frac{4^3}{3^{3/2}}r^3 \approx 12.3168r^3$
Density of a bcc metal:

$$\boxed{d = \frac{(\text{2 atoms per cell})(\text{mass of one atom})}{(\text{volume of one unit cell})} = \frac{(2)(M/N_\text{A})}{a^3} = \frac{(2)(M/N_\text{A})}{\left(4^3/3^{3/2}\right)r^3}}$$

Face-centered

One metal atom (*sphere*) at each *corner point* in a unit cell
One metal atom (*sphere*) at the *center* of each *face* in the unit cell
Total atoms in unit cell = 8 (1/8) + 6 (1/2) = 4
(*four* atoms (radius r) per unit cell (edge length a))
Spheres *touch* along the *face diagonal:* $\sqrt{2}a = 4r$ or $a = \frac{4}{\sqrt{2}}r = \sqrt{8}r$
Volume of the unit cell: $V = a^3 = 8^{3/2}r^3$
Density of a fcc (ccp) metal:

$$\boxed{d = \frac{(\text{4 atoms per cell})(\text{mass of one atom})}{(\text{volume of one unit cell})} = \frac{(4)(M/N_\text{A})}{a^3} = \frac{(4)(M/N_\text{A})}{\left(8^{3/2}\right)r^3}}$$

- **Calculations**
  → Determining the *unit cell* type from the *measured density* and *atomic radius* of metals in the *cubic* system; the *atomic radius* of a metal atom is determined from the crystal type and the edge length

of a unit cell, which are both obtained by x-ray diffraction techniques (see **Major Technique 3** available online).

Example: The *density* of lead is 11.34 g·cm^{-3} and the *atomic radius* is 175 pm. Assuming the unit cell is *cubic,* we can determine the type of Bravais lattice. Using the equations given above, calculate the density of Pb assuming pc, bcc, or fcc Bravais lattices. Results are pc, 8.02 g·cm^{-3}; bcc, 10.4 g·cm^{-3}; fcc, 11.3 g·cm^{-3}. The Bravais lattice is most likely fcc.

3H.6 Ionic Solids

- **Model (r(tetrahedral hole) < r(octahedral hole) < r(cubic hole))**
  - Spheres of *different* radii and *opposite* charges represent cations and anions
  - Larger spheres (*usually* anions) *typically* occupy the unit cell lattice points.
    Smaller spheres (*usually* cations) fill *holes* in the unit cell.
- **Radius ratio [Use rule with caution; there are many exceptions.]**
  - Ratio of radius of the *smaller* sphere to the radius of the *larger* sphere, symbol ρ
  - Defined for ions of the *same* charge number ($z_{\text{cation}} = |z_{\text{anion}}|$)

Radius Ratio–Crystal Structure Correlations

radius ratio ≤ 0.414:	tetrahedral *holes* fill (fcc for *larger* spheres) (*zinc-blende structure* (one *form* of ZnS))
0.414 < radius ratio < 0.732:	octahedral *holes* fill (fcc for *larger* spheres) (*rock-salt structure* (NaCl))
radius ratio ≥ 0.732:	cubic *holes* fill (pc for *larger* spheres) (*cesium-chloride structure* (CsCl))

- **Coordination number**
  - Number of nearest-neighbor ions of *opposite* charge
- **Coordination of ionic solid**
  - Represented as (cation coordination number, anion coordination number)
- **Properties of the *ionic structure* of unit cells**

Zinc blende (see **Figure 3H.32** in the text)

- Radius ratio (ZnS) = $r(\text{Zn}^{2+})/r(\text{S}^{2-})$ = (74 pm)/(184 pm) = 0.40
- S^{2-} ions at the *corners* and *faces* of an fcc unit cell
  (*four* anions (atomic radius r_{anion}) per unit cell (edge length a))
- Zn^{2+} ions in *four* of the *eight* tetrahedral holes in the unit cell
  (*four* cations (atomic radius r_{cation}) per unit cell (edge length a))
- Cation and anion spheres *touch* in the tetrahedral locations.
  Each cation has *four* nearest-neighbor anions, and each anion has *four* nearest-neighbor cations: *(4,4)-coordination.*

Rock salt

- Radius ratio (NaCl) = $r(\text{Na}^+)/r(\text{Cl}^-)$ = (102 pm)/(181 pm) = 0.564
- Cl^- ions at the *corners* and *faces* of an fcc unit cell
  (*four* anions (atomic radius r_{anion}) per cell)
- Na^+ ions in all *four* octahedral holes in the unit cell
  (*four* cations (atomic radius r_{cation}) per cell)
- Cation and anion spheres *touch* along the cell edges (length a).
  Each cation has *six* nearest-neighbor anions, and each anion has *six* nearest-neighbor cations: *(6,6)-coordination.*
- Spheres *touch* along the *edge:* $a = 2\,r_{\text{cation}} + 2\,r_{\text{anion}} = 566$ pm
- Volume of the unit cell: $V = a^3 = 1.81 \times 10^8\ \text{pm}^3 = 1.81 \times 10^{-22}\ \text{cm}^3$
- Density of NaCl: M(58.44 g·mol^{-1}) and d(experimental) = 2.17 g·cm^{-3}

$$\boxed{d = \frac{(4\ \text{NaCl per cell})(M/N_{\text{A}})}{a^3} = \frac{4(58.44/N_{\text{A}})}{(1.81\times10^{-22})} = 2.14\,\text{g·cm}^{-3}}$$

Cesium chloride

- Radius ratio (CsCl) = $r(\text{Cs}^+)/r(\text{Cl}^-)$ = (170 pm)/(181 pm) = 0.939
- Cl^- ions at the *corners* of a pc (*primitive cubic*) unit cell
  (*one* anion (radius r_{anion}) per cell)
- Cs^+ ion at the *center* of the *cube* in the unit cell
  (*one* cation (radius r_{cation}) per cell)
- Cation and anion spheres *touch* along the *body diagonal* of the cell.
  Each cation has *eight* nearest-neighbor anions and each anion has *eight* nearest-neighbor cations: *(8,8)-coordination.*
- Spheres *touch* along the *body diagonal:* $\sqrt{3}\,a = 2\,r_{\text{cation}} + 2\,r_{\text{anion}} = 702$ pm and $a = 405$ pm
- Volume of the unit cell: $V = a^3 = 6.64 \times 10^7\ \text{pm}^3 = 6.64 \times 10^{-23}\ \text{cm}^3$
- Density of CsCl: M(168.36 g·mol^{-1}) and d(experimental) = 3.99 g·cm^{-3}

$$\boxed{d = \frac{(1\ \text{CsCl per cell})(M/N_{\text{A}})}{a^3} = \frac{1(168.36/N_{\text{A}})}{(6.64\times10^{-23})} = 4.21\,\text{g·cm}^{-3}}$$

- **Calculations**
  - Determining the *ionic structure* in the *cubic* system from *ionic radii* using the *radius ratio*
  - Determining the *density* of the *ionic solid* from the *density* of the *unit cell*
    Note: Usually within 10% of the experimental value