Molecular vs. Continuum

- Classical fluid mechanics (i.e., A&AE 511) treats a gas as an infinitely divisible substance, a *continuum*.

- As a consequence of continuum assumption, each fluid property is assumed to have a definite value at each point in space. Density, temperature, velocity, and so on, are considered to be functions of position and time.

- For most of gas dynamics phenomena experienced by humans (1 atm pressure, room temperature, length scales ~ 1 m), continuum hypothesis is valid.

- However, many modern engineering applications (space flight, micro-electro-mechanical devices) occur at conditions where more detailed molecular description of the structure of gaseous matter is necessary.
Early Theories of Matter

Greek philosophers believed that matter consisted of four basic elements: earth, air, water, and fire. Aristotle (384-322 BCE) proposed that elements also contained two of the following qualities: heat, cold, moisture, and dryness. For example, fire was hot and dry; water was cold and moist; air was hot and moist; and earth was cold and dry. Because qualities could vary, it was possible to change lead into gold (alchemy).

Some dissenting Greek philosophers argued that motion is impossible unless there is an empty space into which a moving body could move. Thus arising the hypothesis that all matter consists of very small particles separated by void.
Early Atomistic Ideas

- Spheres with hooks.

- Intermeshing gears.
Early Theories of Gases

• Robert Boyle (1627-1691): \( pV = \text{Const} \)

Boyle's atomistic explanations for air pressure:

\textit{repulsion theory} - air is composed of particles that repel each other, like coiled-up pieces of wool or springs.

\textit{kinetic theory} - air is composed of moving particles that push each other away by impacts.

• Daniel Bernoulli (1700-1782) formulated a quantitative kinetic theory. He derived Boyle's law for gas pressure by showing that pressure is proportional to kinetic energy of particles.
Early Theories of Gases

- Joseph Gay-Lussac (1778-1850) formulated Law of Combining Volumes: “The compounds of gaseous substances with each other are always formed in simple ratios by volume”.

\[ \text{Chemical combinations always occur in simple proportions:} \]
\[ 2\text{H}_2 + \text{O}_2 \rightarrow 2\text{H}_2\text{O} \]
Early Theories of Gases

● Amedeo Avogadro (1776-1856) explained Gay-Lussac's Law of Combining Volumes: “Equal volumes of gases at equal pressure and temperature contain the same number of molecules”. This radical idea wasn't accepted until 1860s.

At 0°C and 1 atm, 22.4 L contain 1 mol of any gas

\[ 1 \text{ mol} = 6.022 \times 10^{23} \text{ molecules}. \]
Molecular Hypothesis

• John Dalton (1766-1844)'s Atomic Theory:
  ▶ All matter is composed of extremely small particles called atoms.
  ▶ All atoms of a given element are identical, having the same size, mass, and chemical properties. Atoms of a specific element are different from those of any other element.
  ▶ Atoms cannot be created, divided into smaller particles, or destroyed.
  ▶ Different atoms combine in simple whole-number ratios to form compounds.
  ▶ In a chemical reaction, atoms are separated, combined, or rearranged.

• Molecular hypothesis officially closed book on alchemy: if each element is made of different atoms then it's impossible to make gold out of lead.
Kinetic Theory of Gases

• Kinetic theory attempts to explain the *macroscopic* observable properties of gases (pressure, temperature) by considering its *microscopic* properties (molecular composition and motion).

• Basic postulates:
  
  – A *molecule* is the smallest particle of a pure chemical substance that still retains its composition and chemical properties.
  
  – The gas consists of molecules which are in constant, random motion. Thus the name *kinetic theory*.
  
  – Molecules exert forces on one another only during collisions (*ideal gas*).
  
  – Average distance separating the gas particles is large compared to their size (*dilute gas*). Only binary collisions are probable.
  
  – Interactions between molecules are usually described by classical mechanics (quantum-mechanical and relativistic effects are negligible).
Statistical Nature of the Theory

- We cannot possibly follow every molecule and calculate its exact path, thus we are confined to statistical description in terms of probabilities of finding molecules in a particular state.

- Macroscopic gas properties such as density, pressure and temperature are averages.

- A macroscopically small volume is a volume just small enough so that for experimental purposes at hand it can be treated as indefinitely small.
Statistical Nature of the Theory

• **Instantaneous average** is average over a macroscopically small volume at some moment of time.

• **Time average** is established by summing the appropriate properties of the molecules in the volume element over an extended time interval.

• **Ensemble average** is an instantaneous average taken over the molecules in corresponding volume elements in an indefinitely large number of similar systems.