February 3, 2016 Physics 132 Prof. E. F. Redish

■ **<u>Theme Music:</u> Zimmer & Howard**

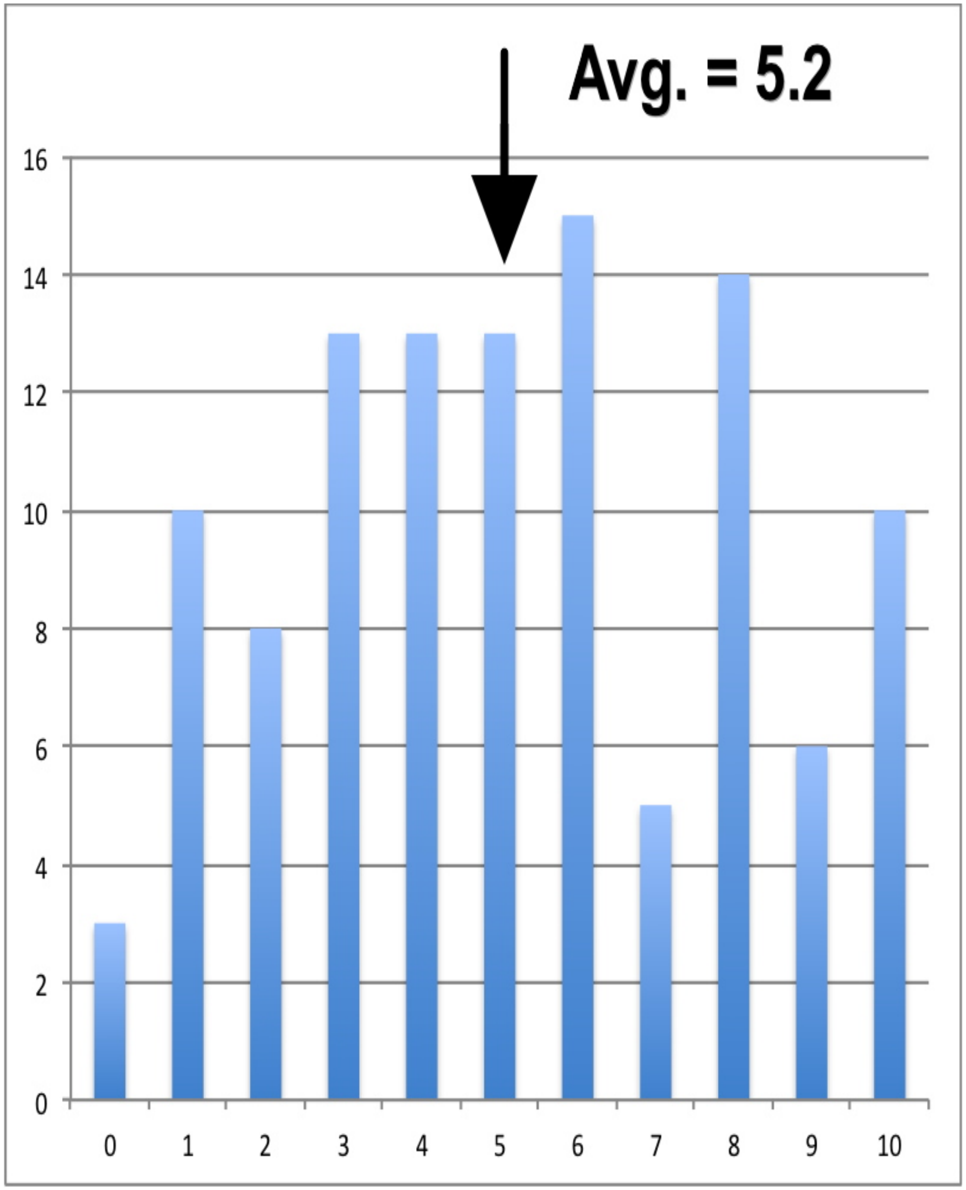
Agent of Chaos **(from The Dark Knight)**

■ **<u>Cartoon:</u> Mike Peters**

Mother Goose & Grimm

Quiz 1

	#1	#2	#3
a	19%	6%	28%
b	61%	82%	57%
c	24%	40%	65%
d	75%	4%	25%
e	56%	85%	61%
f	68%	78%	45%



Changing our assumptions

- In each of our examples above,
  we imagined a gas (or two gases) reacting
  in a closed container.
- While this is plausible – and relevant for many mechanical engineering example (the piston in the engine of an automobile, for example) in most biological situations,
  reactions occur at a constant pressure
  (in the open), not at a constant volume.
- What does that do to our energy conservation?

Why we need enthalpy

- When chemicals react in the open, they do so in a pressurized environment. They will expand or contract in order to maintain their pressure.
- In so doing, they will either do work on their environment or have work done on them.
- This will change the energy balance equation.

Recap: Partial pressure

- In a gas, pressure is produced by molecules hitting any surface introduced into it.

$$pV = Nk_BT \qquad p = nk_BT \qquad n = \frac{N}{V}$$

- If T is constant, p is directly proportional to n – the number density.
- Mixing many gases together, the pressure just adds the result of each molecule hitting the wall.
- The total p is the sum of the *partial pressures*.

$$p = p_1 + p_2 + ... = (n_1 + n_2 + ...)k_BT$$

Foothold ideas: Energy

- Kinds of energy (?)
  - Kinetic
  - Potential
  - Thermal
  - Chemical
- First law of thermodynamics
  - Conservation of total energy

Internal energy

Thermal energy entering

Work done on the rest of the world

$$\Delta U_{\text{int}} = Q - W$$

Energy needed to add internal energy at constant pressure (Enthalpy)

$$\Delta H = \Delta U + p\Delta V$$

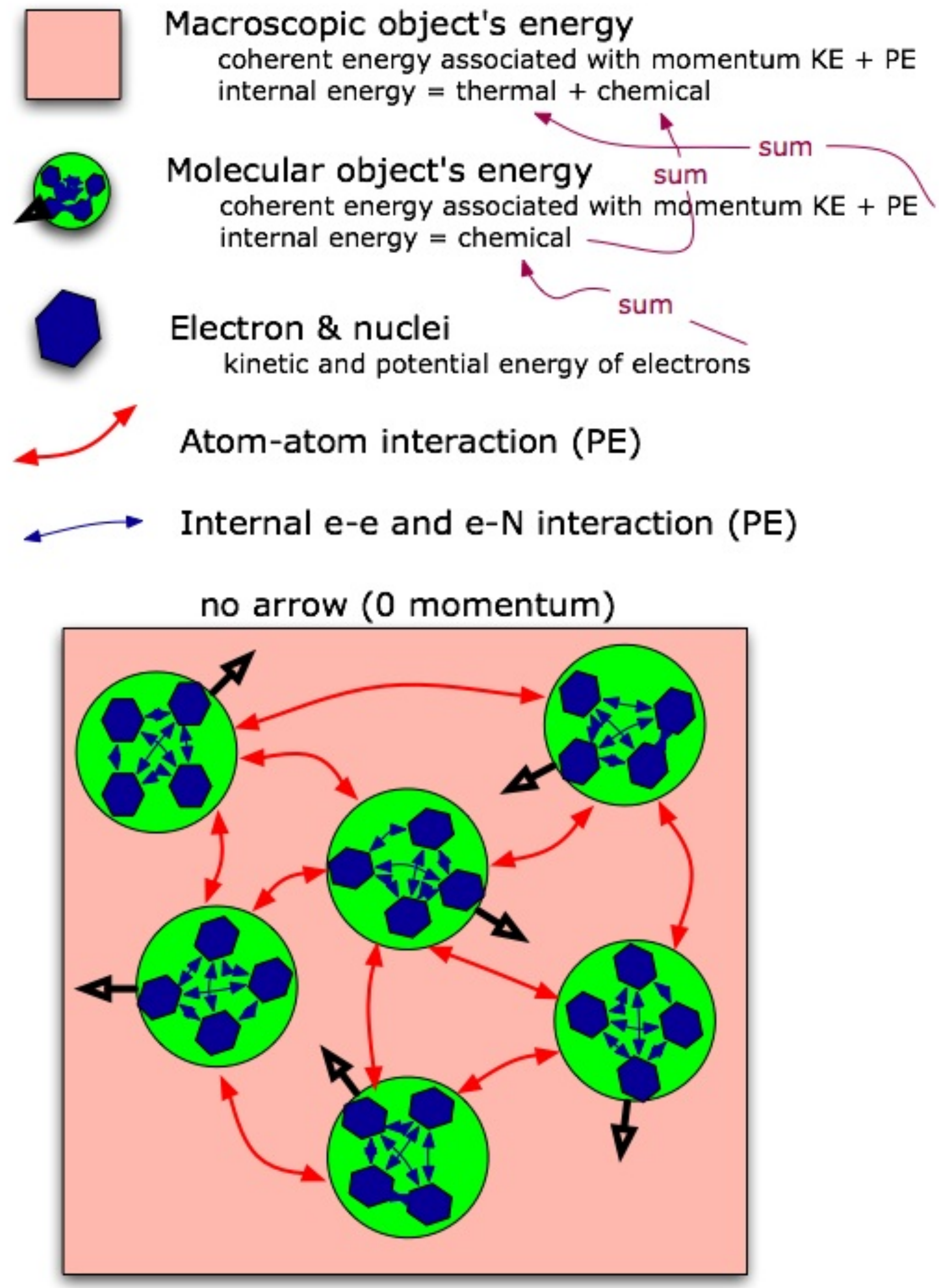
We need to create a system schema for describing energy

- Consider a macroscopic object.
- Construct a system schema representation that shows the various places energy can reside in its internal structure (where "internal energy" can live).

Zooming in on internal energy

(a generalization of the system schema)

As the system moves, energy is moving randomly among these locations (“bins”).



Foothold ideas: Thermal Equilibrium & Equipartition

- ***Degrees of freedom*** – places energy can reside in a system.
- ***Thermodynamic equilibrium is dynamic*** – Changes keep happening, but equal amounts in both directions.
- ***Equipartition*** – At equilibrium, there is the same energy density in all space and in all DoFs – on the average.

Foothold ideas: Connecting micro and macro

- *Microstate* – A specific arrangement of energy among all the degrees of freedom of the system
- ***Different microstates may not be distinguishable when you are looking at many molecules*** – At the macro level (even as small as nm^3) some microstates look the same.
- *Macrostate* – A specification of things we care about at the macro level: pressure, temperature, concentration.

Foothold ideas: Entropy

- ***Entropy*** – an extensive* measure of how well energy is spread in an object.
- Entropy measures
  - The number of microstates in a given macrostate

$$S = k_B \ln(W)$$

  - The amount that the energy of a system is spread among the various degrees of freedom
- Change in entropy upon heat flow

$$\Delta S = \frac{Q}{T}$$

Foothold ideas: The Second Law of Thermodynamics

- Systems composed of a large number of particles spontaneously move toward the thermodynamic (macro)state that correspond to the largest possible number of particle arrangements (microstates).
  - The 2nd law is probabilistic. Systems show fluctuations – violations that get proportionately smaller as N gets large.
- Systems that are not in thermodynamic equilibrium will spontaneously transform so as to increase the entropy.
  - The entropy of any particular system can decrease as long as the entropy of the rest of the universe increases more.
- The universe tends towards states of increasing chaos and uniformity. (Is this contradictory?)