- **<u>Theme Music:</u> Duke Ellington**
  Take the A Train
- **<u>Cartoon:</u> Lynn Johnson**
  For Better or for Worse

Foothold principles: Newton's Laws

- Newton 0:
  - An object responds **only** to the forces it feels and only at the instant it feels them.
- Newton 1:
  - An object that feels a net force of 0 keeps moving with the same velocity (which may = 0).
- Newton 2:
  - An object that is acted upon by other objects changes its velocity according to the rule

$$\vec{a}_A = \vec{F}_A^{net} / m_A$$

- Newton 3:
  - When two objects interact the forces they exert on each other are equal and opposite.

$$\vec{F}_{A\to B}^{type} = -\vec{F}_{B\to A}^{type}$$

Foothold ideas:
Kinetic Energy and Work

- Newton's laws tell us how velocity changes. The Work-Energy theorem tells us how speed (independent of direction) changes.
- Kinetic energy = $\frac{1}{2}mv^2$
- Work done by a force = $F_x \Delta x$ or $F_{||}\Delta r$ (part of force || to displacement)
- Work-energy theorem: $\Delta(\frac{1}{2}mv^2) = F_{||}^{net}\ \Delta r$ (small step)

$$\Delta(\tfrac{1}{2}mv^2) = \int_i^f F_{||}^{net}\ dr$$ (any size step)

Foothold ideas: Potential Energy

- The work done by some forces only depends on the change in position. Then it can be written

  $$\vec{F} \cdot \Delta\vec{r} = -\Delta U$$

  U is called a *potential energy*.

- For gravity, $U_{gravity} = mgh$

  For a spring, $U_{spring} = \frac{1}{2} kx^2$

  For electric force, $U_{electric} = k_C Q_1 Q_2 / r_{12}$

- Potential to force: $$\vec{F} = -\frac{\Delta U}{\Delta\vec{r}} = -\left(\frac{\partial U}{\partial x}\hat{i} + \frac{\partial U}{\partial y}\hat{j} + \frac{\partial U}{\partial z}\hat{k}\right) = -\vec{\nabla} U$$

  The force associated with a PE at a given place points "downhill" – in the direction where the PE falls the fastest.

Foothold ideas: Energy

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

Internal energy

Thermal energy entering

Work done on the rest of the world

$$\Delta U = Q - W$$

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

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

Foothold ideas: Bound states

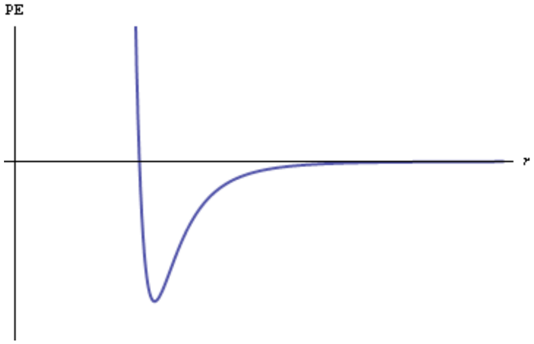
- When two objects attract, they may form a *bound state* – that is, they may stick together.
- If you have to do positive work to pull them apart in order to get to a separated state with KE = 0, then the original state was in a state with negative energy.

Foothold ideas: Inter-atomic interactions

- The interaction between atoms arises from the combination of the electrical forces of its components (electrons and nuclei).
  - It can be quite complex and involve electron sharing and chemical bonds.
  - The complexity arises from the quantum character of electrons.
- Despite this complexity, a simple potential model summarizes many features of a two-atom interaction.

Foothold ideas: Inter-atomic potentials

- The interaction between neutral atoms includes an attraction at long-range that arises from the fluctuating charge distribution in each atom; the PE behaves like $1/r^6$.
- When the atoms are pressed close, they repel each other strongly; both because the +nuclei repel and because of the Pauli principle (two electrons cannot be in the same state).
- Two commonly used models are:
  - The Lennard-Jones potential ($A/r^{12}-B/r^6$)
  - The Morse potential (exponentials)



Foothold ideas:
Energy conservation with chemical energy

- Consider the reaction of a gas of A and B molecules that react (fully) to C and D molecules A + B → C + D
  - If the initial and final states both have the two molecules far apart, $U_{\mathrm{AB}} \sim U_{\mathrm{CD}} \sim 0$.

$$U^i_{thermal} + U^i_{chemical} = U^f_{thermal} + U^f_{chemical}$$

$$\Delta U_{thermal} + \Delta U_{chemical} = 0$$

Foothold ideas:
Thermal Equilibrium & Equipartition

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

Foothold ideas: Enthalpy

- When a chemical reaction takes place at a **constant *T* and *p*** (especially in a gas), the gas may have to do work to "make room for itself". This affects the energy balance between the chemical energy change and the thermal energy change.
- Define *enthalpy, H*

$$\Delta H = \Delta U_{thermal} + \Delta U_{chemical} + p\Delta V$$

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

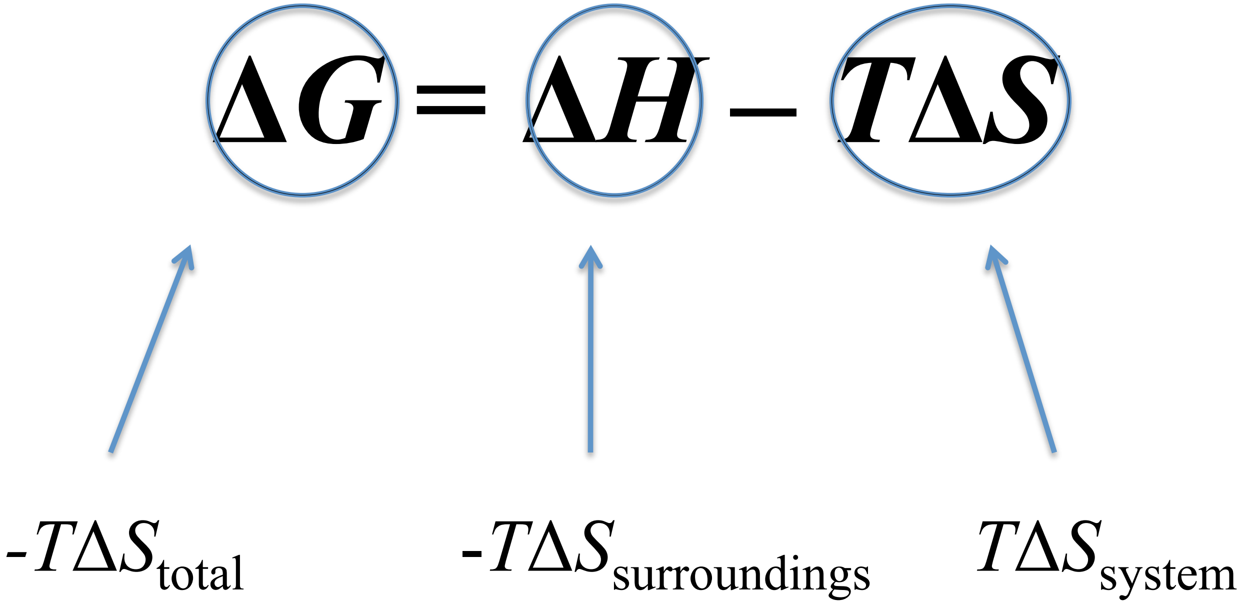
Foothold ideas:
The Second Law of Thermodynamics

- 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?)

Foothold ideas: Transforming energy

- Internal energy: thermal plus chemical ΔU
- Enthalpy: internal plus amount needed to make space at constant *p* $\Delta H = \Delta U + p\Delta V$
- Gibbs free energy: enthalpy minus amount associated with raising entropy of the rest of the universe due to energy dumped $\Delta G = \Delta H - T\Delta S$
- A process will go spontaneously if $\Delta G < 0$.

Spontaneity…



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

$-T\Delta S_{\text{total}}$ $-T\Delta S_{\text{surroundings}}$ $T\Delta S_{\text{system}}$

The sign of the Gibbs Free Energy change indicates spontaneity!

$\Delta G < 0 \rightarrow \Delta S_{\text{total}} > 0 \rightarrow$ spontaneous

$\Delta G > 0 \rightarrow \Delta S_{\text{total}} < 0 \rightarrow$ not spontaneous

Foothold ideas: Energy distribution

- Due to the randomness of thermal collisions, even in (local) thermal equilibrium a range of energy is found in each degree of freedom.
- The probability of finding an energy E is proportional to the Boltzmann factor

$$P(E) \propto e^{-E/k_B T} \quad \text{(for one DoF)}$$

$$P(E) \propto e^{-E/RT} \quad \text{(for one mole)}$$

- At 300 K, $k_B T \sim 1/40$ eV

$$N_A k_B T = RT \sim 2.4 \text{ kJ/mol}$$

The Boltzmann probability

- The probability of finding an additional energy ΔE in a DoF is proportional to the number of ways that that energy can be distributed, W.
- The overall probability has to be normalized so that the sum (integral) over all energies is 1.

$$P(\Delta E,T) = P_0 W(\Delta E,T) e^{-\Delta E / k_B T}$$

Foothold ideas:
Exponents and logarithms

- Power law: $f(x) = x^2 \quad g(x) = Ax^7$
  a variable raised to a fixed power.
- Exponential: $f(x) = e^x \quad g(N) = 2^N \quad h(z) = 10^z$
  a fixed constant raised to a variable power.
- Logarithm: the inverse of the exponential.

$$x = e^{\ln(x)} \qquad x = \ln\left(e^x\right)$$

$$y = 10^{\log(y)} \qquad y = \log\left(10^y\right)$$

$$\log(2) = 0.3010$$
$$\log(e) = 0.4343$$
$$2^N = \left(10^{0.3010}\right)^N \approx 10^{0.3N}$$
$$e^x = \left(10^{0.4343}\right)^x \approx 10^{0.4x}$$
$$2^N = B$$
$$N \log 2 = \log B \Rightarrow N = \frac{\log B}{\log 2}$$

Logs convert multiplying to adding!

Foothold ideas:
Charge – A hidden property of matter

- Matter is made up of two kinds of electrical matter (positive and negative) that usually cancel very precisely.
- Like charges repel, unlike charges attract.
- Bringing an unbalanced charge up to neutral matter polarizes it, so both kinds of charge attract neutral matter
- The total amount of charge (pos – neg) is constant.

Foothold ideas: Conductors and Insulators

- Insulators
  - In some matter, the charges they contain are bound and cannot move around freely.
  - Excess charge put onto this kind of matter tends to just sit there (like spreading peanut butter).
- Conductors
  - In some matter, charges in it can move around throughout the object.
  - Excess charge put onto this kind of matter redistributes itself or flows off (if there is a conducting path to ground).

Foothold idea: Coulomb's Law

- All objects attract each other with a force whose magnitude is given by

$$\vec{F}_{q\to Q} = -\vec{F}_{Q\to q} = \frac{k_C qQ}{r_{qQ}^2}\hat{r}_{q\to Q}$$

- k_C is put in to make the units come out right.

$$k_C = 9\times 10^9 \text{ N-m}^2/\text{C}^2$$

Foothold ideas:
Energies between charge clusters

- Atoms and molecules are made up of charges.
- The potential energy between two charges is

$$U_{12}^{elec} = \frac{k_C Q_1 Q_2}{r_{12}}$$

No vectors!

- The potential energy between many charges is

$$U_{12\ldots N}^{elec} = \sum_{i<j=1}^{N} \frac{k_C Q_i Q_j}{r_{ij}}$$

Just add up all pairs!

Foothold idea:
Fields

- *Test particle*
  - We pay attention to what force it feels.
    We assume it does not have any affect on the source particles.
- *Source particles*
  - We pay attention to the forces they exert and assume they do not move.
- *Physical field*
  - We consider what force a test particle would feel if it were at a particular point in space and divide by its coupling strength to the force. This gives a vector at each point in space.

$$\vec{g} = \frac{1}{m}\vec{W}_{E\to m} \qquad \vec{E} = \frac{1}{q}\vec{F}_{\text{all charges }\to q} \qquad V = \frac{1}{q}U^{elec}_{\text{all charges}\to \text{q}}$$

Foothold ideas:
Electric potential energy and potential

- The potential energy between two charges is

$$U_{12}^{elec} = \frac{k_C Q_1 Q_2}{r_{12}}$$

- The potential energy of many charges is

$$U_{12\ldots N}^{elec} = \sum_{i<j=1}^{N} \frac{k_C Q_i Q_j}{r_{ij}}$$

- The potential energy added by adding a test charge *q* is

$$\Delta U_q^{elec} = \sum_{i=1}^{N} \frac{k_C q Q_i}{r_{iq}} = qV$$

= the voltage at the position of the test charge

Units

- Gravitational field
  units of g = Newtons/kg
- Electric field
  units of E = Newtons/C
- Electric potential
  units of V = Joules/C = Volts
- Energy = qV so $e\Delta V$ = the energy gained by an electron (charge $e = 1.6 \times 10^{-19}$ C) in moving through a change of ΔV volts.
  1 eV = 1.6×10^{-19} J

Representations

- Representing E
  - Arrows (length shows $|E|$)
  - Arrows (fixed length, color or width shows $|E|$)
  - Field lines (show direction only)
  - Field lines (color shows $|E|$)
- Representing V
  - 1D: Graph
  - 2D: Isoclines (lines of equal value)
  - 3D: Equipotential surfaces (surfaces of = value)

Foothold ideas: Electric charges in materials

- The electric field inside the body of a static conductor (no moving charges) is zero.
- The entire body of a static conductor (no charges moving through it) is at the same potential.
- The average electric field in an insulator
  is reduced (due to the polarization of the material by the field) by a factor that is a property
  of the material: the dielectric constant, κ.
  (Sometimes written in biology as ε) Since κ is the ratio of two fields, it is dimensionless.