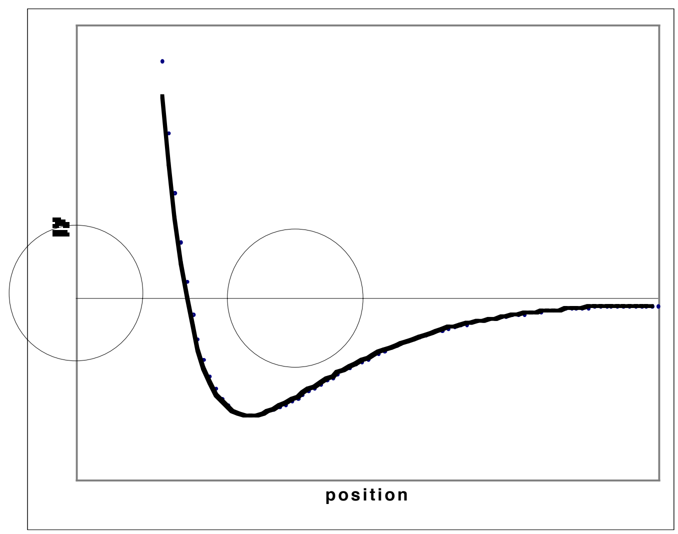
Notes on Thermodynamics, I:

Thermodynamics is the study of the *internal mechanical energy* of macroscopic bodies. A macroscopic body is one that can, in principle, be seen by shining light on it. Macroscopic bodies consist of huge numbers (e.g., 10^{20} to 10^{30}) of atoms. The mechanical energy (kinetic energy plus potential energy) of a collection of elementary particles (electrons and quarks) can be organized into the following pieces: ME of the CM (that corresponds to a *translation* of the collection as a whole) plus ME due to coherent motion around the CM (such as a rotation, or a wave, or the flow of a fluid) plus ME due to incoherent atomic level motion. The first two contributions require that the atoms move together coherently over distances that can be measured by macroscopic devices (meter sticks or motion sensors, for example). The latter contribution cannot be seen—it is *internal* to the body. Nonetheless, internal energy can be measured and the manner in which it is distributed in a body can be inferred.

Here are a few fundamental facts that are essential to keep in mind as you study thermodynamics:

- When two atoms "collide" energy is always transferred from the one that has higher energy to the one that has lower energy. This is so because in any interaction between two atoms energy *and* momentum have to be conserved, and the latter can't be if energy goes from the lower energy atom to the higher.
- The interactions between two macroscopic bodies always involve some degree of *irregularity*. Irregular interactions at the atomic level always convert coherent atomic motion into incoherent motion.
- The internal incoherent motions of atoms have macroscopic consequences. A lot of what we call "thermodynamic" properties of bodies can be understood from the interatomic potential energy graph. See the figure to the right. The circles roughly represent two atoms. The curve is the potential energy of interaction for two atoms as a function of the atoms' separation. When the atoms get too close they repel because their electrons obey the Pauli exclusion principle. When they are farther apart they attract because of the electrical attraction between negatively charged electrons and positively charged nuclei.



- According to the rules of *quantum mechanics*, **all bodies that are confined to a finite region of space must be moving**. The smallest amount of kinetic energy a confined body can have is of the order of $10^{-68}/mL^2$ joules, where m is the mass of the body (in kg) and L is the length of the region of confinement. A 1 kg mass confined to a region of about 1 m has a minimum KE of about 10^{-68} J. That's such a preposterously small value that we don't notice it in the macroscopic world. On the other hand, an electron ($m \approx 10^{-30}$ kg) confined inside an atom ($L \approx 10^{-10}$ m) must have a minimum KE of about 10^{-18} J. This seems like a small value also, but it can actually be measured quite readily. (It's equivalent to the energy an electron would get if it was pushed across a flashlight battery—an electric push of a few volts.)
- Quantum mechanics also says that **the mechanical energy of all confined bodies actually can take on only certain allowed values**. The energy difference between two successive allowed values is also of the order of $10^{-68}/mL^2$. Again, because this value is so small for macroscopic bodies we don't see that energy changes come in discrete jumps. It looks, in the macroscopic world, as if energy

changes can take on any value we please. But, the consequences of discreteness of energy levels in the microscopic world are profound. The allowed energies for the motion of protons and neutrons in a nucleus are separated by $\Delta E \approx 10^{-11}$ J, because $m \approx 10^{-27}$ kg, and $L \approx 10^{-15}$ m. The allowed energies for the motion of electrons in an atom are separated by $\Delta E \approx 10^{-18}$ J (see above). The allowed energies for the vibrational motion of atoms in a molecule or in a solid (which is just a BIG molecule) are separated by $\Delta E \approx 10^{-22}$ J ($m \approx 10^{-26}$ kg, $L \approx 10^{-10}$ m). The allowed energies for the rotation of atoms in a molecule are separated by $\Delta E \approx 10^{-23}$ J (*m* is a little bigger than for atoms vibrating) and for the translation of atoms in a 1 cc volume $\Delta E \approx 10^{-40}$ J. **At room temperature, the energy of two atoms colliding is about 10^{-21} J**, which is bigger than any of the latter three example energy differences. Thus, at room temperature, it is possible to put energy via collisions into atomic translations, molecular rotations, and atomic vibrations, but it is impossible to cause a change in motion of an electron in an atom or of the protons and neutrons in a nucleus. The available energy is too small by a factor of about 1000 for atomic electron excitation, so to do that would require a temperature of about 1000 times room temperature! For a nuclear motion change it would take a temperature of about 10^{12} or so times room temperature!!! As far as thermodynamics at ordinary temperatures is concerned, we can completely ignore electrons in atoms and nucleons in nuclei. Those parts of the internal energy of matter are unaffected by atomic collisions are thus as good as not there.

- There are internal states of motion called *equilibrium* states. This means that if we calculate the average volume or pressure or density or any other macroscopic property due to incoherent atomic motion, nothing changes in time (except for small fluctuations).
- *Thermal equilibrium* in a body is defined as the condition that average internal energy per atom is the same everywhere in the body. Two bodies are in thermal equilibrium if the average internal energy per atom is the same in the two bodies.
- *Thermal contact* is the condition that two macroscopic bodies are close enough to each other that internal energy can be exchanged between the two by collisions of the atoms at the interface separating the two bodies.
- ***Temperature* is a measure of the average internal energy per atom of a macroscopic body**. We choose the convention that temperature increases as average internal energy per atom increases.
- When two bodies at different temperatures are placed in thermal contact they will exchange internal energy until the average internal energy per atom is the same in both bodies. At that point they are in thermal equilibrium—and they are at the same temperature. This idea allows us to define a *thermometer*. A thermometer is small (so it doesn't affect the internal energy of another body in which it is in thermal contact very much) and one of its macroscopic properties (such as volume or pressure or electrical conductivity …) is used to measure temperature.