

3.1: Heat and Work

We've seen how to calculate—at least in principle, although our techniques were primitive and difficult to use—the entropy $S(E, V, N)$. We've also argued (“the booty argument”, section 2.7.1) that for most systems entropy will increase monotonically with energy when V and N are fixed. Thus we (can)/(will always be able to) invert the function to find energy as a function of entropy, volume, and number:

$$E(S, V, N). \quad (3.1.1)$$

Recall that V and N are just stand-ins as representative mechanical parameters.

But how can we measure entropy? Walk into any laboratory and the experimentalist there will say “I have thermometers for measuring temperature. I have resistors, ammeters, and voltmeters, and I have a procedure for using these instruments to measure the heat flowing into a sample. I have calibers for measuring volume and manometers for measuring pressure. But I have no instrument to measure the number of microstates consistent with a given macrostate.” Although we have produced a conceptual definition of entropy, we need also an *operational definition* of entropy.

An “operational definition” defines the target word, not in terms of other words, but in terms of a procedure that produces a decision or a numerical value concerning that target word. For example, an operational definition for the word tuberculosis is “a disease marked by wasting, cough, fever, and formation of small cheesy lumps in the lungs”. In contrast, a conceptual definition is “a disease caused by the bacillus bacterium *Mycobacterium tuberculosis*”. The operational definition tells you how to diagnose the disease; the conceptual definition tells you what’s going on and suggests a cure. We need to produce an operational definition to go along with our conceptual definition of entropy, and that’s the starting point of this chapter.

Heat:

Change in energy with no change in mechanical parameters =

Change in energy due to temperature difference between system and surroundings =

Heat (absorbed by system) = Q

Configuration work.

Change in energy due to change in mechanical parameters =

Change in energy when system is wrapped in insulating (“no-skid”) walls =

Configuration work (done by system) = W_{conf}

Dissipative work.

Change in energy due to non-equilibrium effects =

Change in energy due to, e.g., shaking, stirring, or running current through the system =

Dissipative work (done by system) = W_{diss}

It is an empirical fact (sometimes called “the second law of thermodynamics”), that dissipative work always increases the energy of the system. Joule the brewer; story about honeymoon at Cascade de Sallanches.

Caution: Heat and work refer to mechanisms for energy *change*, not to types of energy. Do not think that heat goes into a change of kinetic energy (or into “mixed up energy”) whereas work goes into a change of potential energy (or into “ordered energy”).

Any change due to heating could also be done via dissipative work, and there’s no way you could tell the difference. Joule called this “the conversion of work to heat”, although that’s not correct using the modern definitions of “work” and “heat”.

Analogy: You can put money into your bank account through depositing cash or checks, or through an electronic funds transfer. You can take money out of your bank account through these three mechanisms too. But once the money is inside your bank account, you cannot say “This dollar was deposited through cash, while that dollar was deposited through electronic funds transfer.” Once they’re in your account, you can’t distinguish the dollars through the mechanism of entrance. Similarly with energy. You can increase the temperature and energy of a cup of water by putting it near a flame, or by putting it near a high-temperature resistor, or by stirring it rigorously. Given a high-temperature cup of water, there’s no way to tell which of these mechanisms was used.

$$\Delta E = Q + W_{\text{conf}} + W_{\text{diss}} \quad (3.1.2)$$

Problems

3.1 What is heat?

Below is an excerpt from a sixth-grade science textbook. Find at least six errors in the excerpt.

What is heat?

You have learned that all matter is made up of atoms. Most of these atoms combine to form molecules. These molecules are always moving—they have kinetic energy. Heat is the energy of motion (kinetic energy) of the particles that make up any piece of matter.

The amount of heat a material has depends on how many molecules it has and how fast the molecules are moving. The greater the number of molecules and the faster they move, the greater the number of collisions between them. These collisions produce a large amount of heat.

How is heat measured? Scientists measure heat by using a unit called a calorie. A calorie is the amount of heat needed to raise the temperature of 1 gram of 1 water 1 degree centigrade (Celsius). A gram is a unit used for measuring mass. There are about 454 grams in 1 pound.

What is temperature?

The amount of hotness in an object is called its temperature. A thermometer is used to measure temperature in units called degrees. Most thermometers contain a liquid.

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