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Demonstrating Concepts of Statistical Thermodynamics

More on the Maxwell Demon bottle

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The Maxwell Demon bottle (Fig. 1), a device for demonstrating the statistical nature of irreversible processes and the "elusiveness" of the Maxwell Demon, was described in an earlier reference.[1] We have subsequently found that the Demon bottle also serves admirably to demonstrate other basic and equally elusive concepts of statistical thermodynamics.[2] In particular, it can illustrate the nature of entropy, the difference between a work effect and a heat effect, the difference between reversible and irreversible work effects, the mechanical equivalent of heat, and similar intangibles.

Work and Heat

From a microscopic point of view the internal energy of a system of discrete non-interacting particles (for example, a mole of noble gas) is simply the sum of the particle energies or

$$U = \sum_i u_i n_i \tag{1}$$

where U = internal energy of the system, u_i = the energy magnitude of the "i"th quantum level, and n_i = the number of particles in the "i"th level. (The "n_i" are indeterminate (unfortunately) in a mole of gas, and must therefore be replaced by "p_i"s, the probability of finding a particle in the "i" state. Equation (1) then becomes $\langle U\rangle = \sum_i u_i p_i$. This bit of sophistication may be postponed until after the demonstration.)

The derivative of the internal energy must therefore be

$$dU = \sum_i u_i dn_i + \sum_i n_i du_i \tag{2}$$

Equation (2) states that the energy may be changed in two ways, one involving a change in n_i at constant u_i and the other a change in u_i at constant n_i.

Now most of our students have seen and may even remember a classical thermodynamic expression for the derivative of internal energy which also involves two terms, viz.

$$dU = dQ_R - dW_R \tag{3}$$

By analogy, let the terms in equation (2) equal corresponding terms in equation (3). Thus let

$$dQ_R = \sum_i u_i dn_i \tag{4}$$

which we will call a "heat effect," and

$$-dW_R = \sum_i n_i du_i \tag{5}$$

which we will call a "reversible work effect."

Work Effect

The statistical significance of a "work effect" is a change in the magnitude of allowed energy levels without a change in the population or probability of occupancy of the levels.

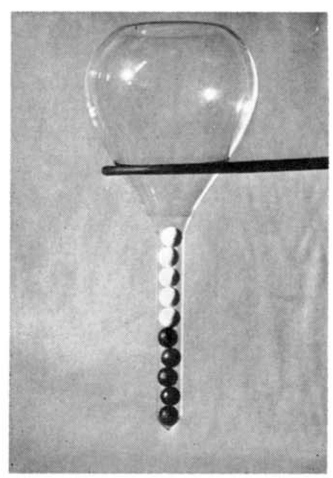

Figure 1. The Maxwell Demon bottle.

Elementary quantum theory tells us that the magnitude of the energy levels can be changed by changing the *external coordinates* of a system. This may be demonstrated with the "Demon" bottle by holding the bottle with the neck down and bringing the black spheres to the bottom of the neck as in Figure 1.

The material in this article was part of a presentation before the May 17, 1965, National Meeting of the American Institute of Chemical Engineers in San Francisco, California.

[1] Sussman, M. V., J. Chem. Educ., **40**, 49 (1963).

[2] I am indebted to Professor Paul Shannon of Dartmouth for suggesting some of the expanded Demon bottle capabilities presented herein.

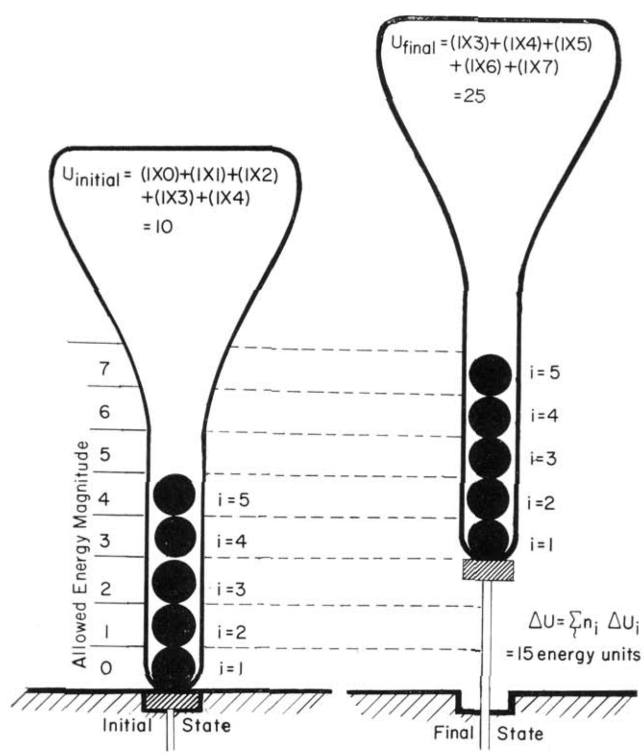

Figure 2. Increasing energy of a system by a reversible work effect.

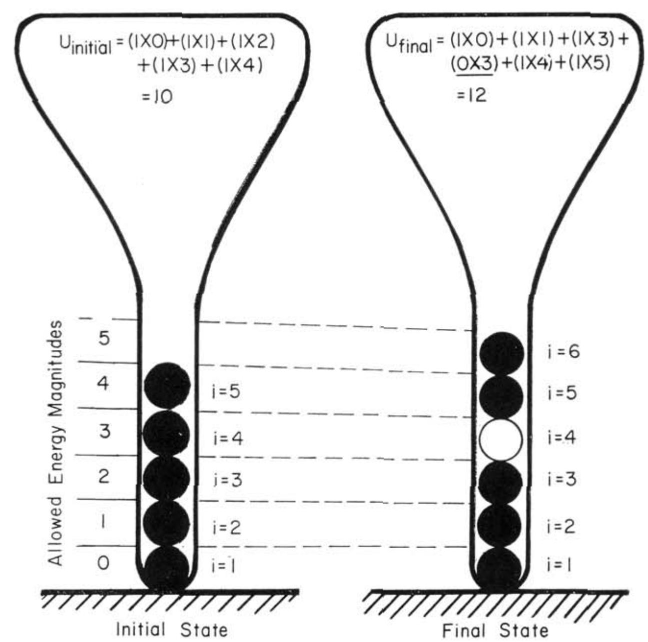

Fig. 3. Increasing energy and entropy of a system by a heat effect. The white ball (which is not counted as a particle) may be in any of six positions. Therefore, we are no longer *certain* of the energy of the system. This lack of certainty or increase in uncertainty is measured by the property called *entropy*.

Let us concentrate our attention on the black spheres only. The black spheres constitute a system of five particles, each in a different allowed energy level. The lowest sphere is in the lowest (potential) energy level and the ones above it are in consecutively higher levels. The end of the bottle neck may be rested on the top of a table which is arbitrarily identified as the potential energy ground state (Fig. 2).

Changing the energy of the system by a "reversible work effect" requires that we change the magnitude of the allowed energy levels without changing their population; and as stated above, this requires a change in the *external coordinates* of the system.

The latter change is accomplished by simply raising the bottle. We thereby change the magnitude of each of the potential energy levels occupied by the black spheres, but do not change the population of these levels. Having raised the system, it is also clear that we have done (classical) work on the system (work done on a system is taken to be negative). In terms of the variables in equation (5), we have changed the values of u_i without disturbing the n_i and hence have changed the energy of the system by an amount equal to $\sum_i n_i \Delta u_i$.

Heat Effect

A "heat effect" changes the population or probability of occupancy of the "ith" energy level without changing the magnitude of that energy level. This is demonstrated with the system of five black particles in the neck of the Demon bottle.

Imagine that a white sphere is interspersed somewhere in between the five black spheres. The white sphere is not a system particle, but represents some mysterious means (a unit of "calorique" fluid?) for making higher energy levels accessible to the system's particles. The interspersion of the white sphere has caused a change in the n_i but has not changed the magnitude of the u_i, and thus has satisfied equation 4 (Fig. 3).

The heat effect is that which makes higher energy levels accessible to the system's particles. The white sphere, interspersed somewhere between the black spheres, has made it possible for some of the system's particles to climb to higher levels than they could reach prior to the heat effect. Obviously, the addition of heat need not be terminated with one white sphere. As more white spheres are added to the system, ever higher energy levels become accessible to the system's particles. The system's particles become more broadly dispersed. One might even say that the "temperature" rises.

Entropy

At this point it is not too difficult to show why a heat effect increases the entropy of a system. Prior to the appearance of the heat effect (the little white sphere which spread the five black spheres to six possible positions), the energy levels in which the system's particles were distributed were precisely known. After the admission of the white sphere, this is no longer true. The five black spheres can be distributed in six possible energy levels. A degree of "uncertainty" has crept into our knowledge of the system. *Entropy is a measure of this uncertainty.* With the addition of one white sphere to the system, the system's entropy has increased to an extent which depends upon the increased number of permutations of five spheres in six positions (6 permutations) as compared to five spheres in five positions (1 permutation), or

$$\Delta S = k(\ln 6 - \ln 1) = 1.79k$$

The Mechanical Equivalent of Heat

The Demon bottle can also be used to show that there is a direct proportionality between the amount of work absorbed by a system and the energy increase of the system; in other words, that a "mechanical equivalent of heat" exists (Fig. 4).

If the magnitudes of the allowed energy levels are designated by the values 0, 1, 2, 3, 4, 5, etc., as shown in the figure, and if a unit work effect is performed when the entire system is displaced upwards a distance corresponding to a unit change in potential energy (Fig. 4), then the ratio between heat and work—that is, the "mechanical equivalent" of heat—is constant. For this system it equals 5.

Other Capabilities

The Demon bottle's capabilities do not end here. They serve to demonstrate the difference between an irreversible and a reversible work effect. For example, a *reversible work effect*, as previously stated, is accomplished by changing the elevation of the entire system without disturbing any of the n_i. An irreversible work effect can be performed by making the same change in elevation, but doing it rapidly (*irreversibly*) *so that the spheres are thrown up into the* body of the flask, and a white sphere becomes interspersed between the column of black spheres. At this point a question as to the entropy effects of reversible and irreversible work effects is easily answered.

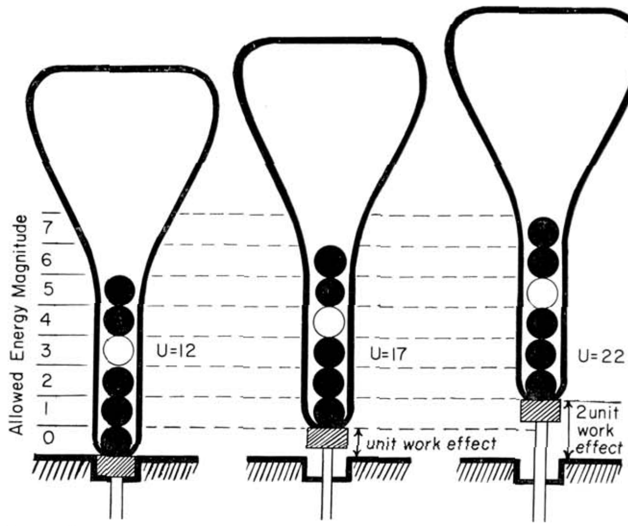

Figure 4. $\Delta U/\Delta W = 5 =$ the mechanical equivalent of heat.

In addition, the particles lined up in the neck of the bottle show interesting analogies to a system of Fermions, electron gas, Fermi levels, etc. These and further ramifications of the Demon bottle are left to readers' imaginations.