

# A SIMPLE MOLECULAR INTERPRETATION OF ENTROPY

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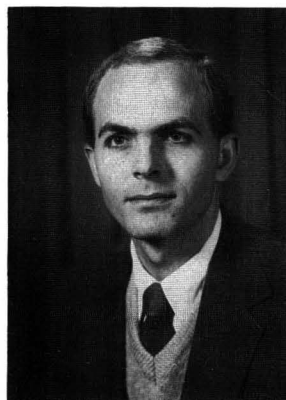
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A CHALLENGE OF MODERN physical science and engineering is to satisfy students as to the connection between fundamental microscopic theories (*e.g.*, gas kinetic theory or quantum mechanics) and macroscopic measurements (*e.g.*, free energy or entropy changes). An approach based on simple notions from gas kinetic theory (thus avoiding the relatively inaccessible approach provided by statistical thermodynamics [1]) has recently been proposed [2] for explaining such macroscopic concepts as heat and work, with specific applications to simple thermodynamic processes. The purpose of this paper is to extend this simple approach so as to provide easily assimilated molecular explanations of entropy changes for such processes.

## INTERNAL ENERGY, HEAT, AND WORK

The most direct link between the microscopic theories and macroscopic measurements is the internal energy  $E$ . For a system of molecules, the total energy is essentially the sum of the individual molecular energies measured relative to some arbitrarily established reference configuration. It can be easily shown [3] that all other macroscopic thermodynamic quantities (*e.g.*, free energy, enthalpy, *etc.*) are simple mathematical extensions of this internal energy which are in some way convenient for the understanding of thermodynamic processes.

A given system of molecules (at thermodynamic equilibrium) is characterized by a temperature  $T$ . It is easy to show [4] that such a system of molecules exists in a set of distributions of energy (translational, vibrational, rotational, electronic) centered around the Boltzmann distribution. This equilibrium distribution of the energy among the molecules is, in a sense, a naturally random arrangement of energy within the physical constraints of fixed particle number and fixed total internal energy. It is the naturally occurring distribution which arises from the most random arrange-



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ment possible.

It has been shown [5] that an additional input of internal energy into a system already in Boltzmann equilibrium results in a rapid "randomization" of the energy among the particles so that a new Boltzmann distribution is formed, characterized by a higher temperature  $T$ . Energy can be added to such a system in two distinct ways, giving rise to the phenomena commonly referred to as heat and work.

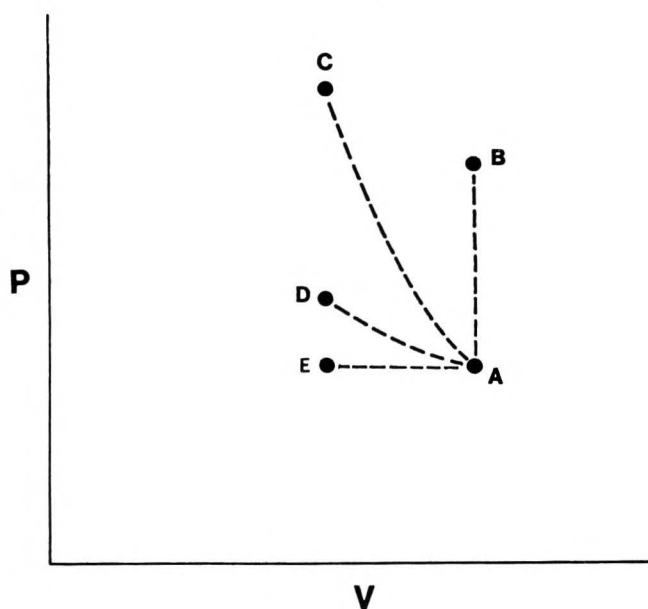
As described previously [2], heat and work are mechanisms for energy transfer processes involving contact between molecules set within unique distributions. Heat is the mechanism for energy transfer between two systems, both of which are in naturally random distributions. Work, on the other hand, is the mechanism of energy transfer between two systems, at least one of which presents itself in some sort of organized distribution (non-Boltzmann).

## ENTROPY

One of the most crucial and least understood of all macroscopic quantities is entropy. Accepting the simple definition of entropy as the measure of the randomness inherent to a system (with reference to a

completely non-random condition), it appears that a molecular understanding of entropy change lies not in the energy characteristics of individual molecules, but in the nature of distributions of energy among systems of molecules. A single molecule may possess internal energy, but it cannot be described as possessing an inherent amount of randomness. Randomness must be measured by the number of different ways in which the internal energy can be distributed among a system of particles. For example, if the total internal energy available is zero, there is only one unique way of distributing it among the particles. More internal energy (corresponding to higher temperatures) results in more possible distributions. Of course, it can be shown [4] that the Boltzmann distribution consists of a very large number of *identical-looking* distributions.

For a gas phase system of molecules, one of the important measurables relating to entropy is the volume. The larger the volume, the more translational energy levels become available for occupation by individual molecules, resulting in more alternatives for constructing distributions. A larger volume, therefore, leads to a higher number of identical-looking naturally random distributions, *i.e.*, a larger entropy.



**FIGURE 1. A PV diagram depicting four typical gas processes.** A-B is a constant volume process resulting in an increase of entropy ( $\Delta T > 0$ ;  $\Delta V = 0$ ;  $\Delta S > 0$ ). A-C is an adiabatic compression resulting in no change in entropy ( $\Delta T > 0$ ;  $\Delta V < 0$ ;  $\Delta S = 0$ ). A-D is an isothermal compression resulting in a decrease in entropy ( $\Delta T = 0$ ;  $\Delta V < 0$ ;  $\Delta S < 0$ ). A-E is an isobaric compression resulting in a larger decrease in entropy than the isothermal case ( $\Delta T < 0$ ;  $\Delta V < 0$ ;  $\Delta S < 0$ ).

Another important factor in changing entropy is the temperature. Raising the temperature is a result of increasing the total amount of internal energy available for distribution, leading to an increase in the number of identical-looking arrangements available to the system of particles. Thus, as with the volume, increase in temperature results in an increase in entropy.

#### ANALYSIS OF SOME SIMPLE THERMODYNAMIC PROCESSES

The four simple gas processes shown in Figure 1 will each be considered separately in order to illustrate the concepts of molecularity relating to heat, work, and entropy as developed above. These processes can be considered as reversible so long as the distributions of energy for the systems are maintained as equilibrium distributions at each infinitesimal step of the process. Otherwise, this constraint need not be invoked.

The constant volume process A-B results when a gas confined to a rigid container with diathermal walls is brought into contact with a bath at a higher temperature. Heat transfer occurs through the walls via the random-random mechanism described above. Notice that there is a "flow" of "randomness" in the direction of the gas. Since the walls are rigid, there is never an organized energy transfer. The internal energy of the gas increases, leading to a new Boltzmann distribution corresponding to a higher temperature  $T$ . Entropy has increased due to the temperature increase (although the volume is constant).

The adiabatic process A-C results when a gas confined to a container with adiabatic walls is compressed. There is no contact with any external randomly distributed system. The compression results in a completely organized energy transfer, *i.e.*, it corresponds to work and results in an increase of internal energy of the system. Upon redistribution of this added energy, the gas achieves a new Boltzmann distribution with higher temperature  $T$ , resulting in a contribution of increased entropy. However, since the volume has decreased, there is an equal contribution of decreased entropy yielding a net result of no change in entropy of the system. This can be seen clearly by noting that since there has been no contact with external random distributions, there can be no change in randomness of the system. Hence the entropy change for this adiabatic process is precisely zero.

The isothermal process A-D results when a gas confined to a container with diathermal walls is compressed. The compression of the box results in or-

ganized energy transfer (work) and would result in a temperature increase except for the fact that the diathermal walls allow for contact between two randomly distributed systems. Since the work transfer tends to push the temperature up, the natural "flow" of "randomness" will be away from the gas towards the external bath. Hence, as far as the system of gas in concerned, the isothermal compression has resulted in a net decrease of randomness, hence a decrease of entropy. This is also evident since the temperature has stayed constant while the volume has decreased.

Finally, the isobaric process A-E results when a gas confined to a container with diathermal walls is compressed and also immersed in a variable temperature bath which is adjusted so as to keep the internal pressure of the gas constant. Again, the compression results in an organized transfer of internal energy (work) tending to increase the temperature. In order for the system to retain constant pressure, however, it is necessary for the increased internal energy to escape via the only route available to it, *i.e.*, the random distribution contact with the external bath. Not only must there be such a contact, but the bath must be adjusted so that the temperature actually decreases. This results in a doubly intense outward "flow" of internal energy via the random distribution mechanism (heat). Hence, the entropy of the system actually decreases more than in the isothermal case. Also, since both the volume *and* temperature decrease for this process, it is clear that the entropy decrease is greater than for the previous case.

Of course, all of these examples have been previously described [2] in terms of pressure effects. The purpose of this set of descriptions has been to extend the gas kinetic ideas to the very difficult concept of entropy.

## CONCLUSION

Definitions of internal energy allow for direct connection to the macroscopic thermodynamic quantities commonly sought by scientists and engineers. The aim of this work has been to demonstrate a simple connection between molecularity (as contained in gas kinetic theory of distributions) and macroscopic quantities such as entropy. It has been shown that entropy, defined as a measure of randomness relative to some reference condition, can be easily interpreted in terms of the distributions and how they change. "Flow" of "randomness" due to different interactions between systems clearly helps to explain entropy changes. While this approach may not simplify the actual calculations required in applications of thermodynamics, it is hoped that it provides a satisfying semi-quantitative explanation of the inherent connection between

molecular mechanics and macroscopic thermodynamic quantities.

## REFERENCES

1. See, for example, N. Davidson, *Statistical Mechanics*, McGraw-Hill, 1962.
2. B. A. Waite, "A Gas Kinetic Explanation of Simple Thermodynamic Processes," *J. Chem. Educ.*, **62** (March), 1985, 224-227.
3. See, for example, I. M. Klotz and R. M. Rosenberg, *Chemical Thermodynamics*, Benjamin, 1972, 128-130.
4. B. A. Waite, "Equilibrium Distribution Functions: Another Look," *J. Chem. Educ.*, **63** (Feb.) 1986, 117-120.
5. See, for example, D. Hinds, D. D. Parrish, and M. A. Wartell, Jr., "Modelling Molecular Velocity Distributions," *J. Chem. Educ.*, **55** (October), 1978, 670. □

## REVIEW: Engines, Energy, Entropy

Continued from page 93.

drawings with clever poems on most pages), to the ideas and results of the great thermodynamicists of the 19th Century. Further, everything is given to accomplish the essential calculations for thermal processes of all types. Thus, anyone with college level experience and intelligence can calculate the efficiencies of the various automotive engine and heat pump cycles without knowing either logarithms or integration beforehand—even their basics are included.

This is not to say that the book is superficial or incomplete (except that it is restricted to constant-composition systems). The order of contents is ancient observations, temperature, systems and states, work, heat, cycles (including Carnot's), energy, heat engines, entropy, and followed by appendices on mechanical properties, logarithms, entropy as a property, atomic weights and symbols. Each chapter has useful and enjoyable worked examples and problems whose answers are given in the back. I found the introduction of entropy quite nice since energy had previously been revealed as a quantity we use merely for keeping track of observations in a special way, and the distinction of heat and work had been carefully established. Then the desirability for having another state property of the special form  $\delta q/T$  could be easily justified by several rigorous, but simple and novel, physical processes and mathematical relationships. Unlike the discussions of some others, I found the portions devoted here to the treatments of temperature scales, pure component phase behavior and thermodynamic cycles to be interesting and in excellent balance with the more intriguing historical, mathematical and molecular discussions. I would expect the book to be challenging to students, but also