

Removing the Mystery of Entropy and Thermodynamics — Part I

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Removing the Mystery of Entropy and Thermodynamics – Part I

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This is the introductory part of a five-part series. Parts II-V will elaborate considerably on the material presented here.

Energy and entropy are centerpieces of physics. Energy is typically introduced in the study of classical mechanics. Although energy in this context can be challenging, its use in thermodynamics and its connection with entropy seem to take on a special air of mystery. In this five-part series, I pinpoint ways around key areas of difficulty to reduce that mystery. In Part I, the focus is on building an understanding of fundamental ideas of thermodynamics, including its connection with mechanics, and how entropy is defined and calculated. A central thread is that energy tends to spread within and between macroscopic objects, and this spreading is a surrogate for entropy increase. Specific questions are posed and answered, building on foundations laid in prior articles.^{1–8} Parts II-V elaborate considerably on the ideas introduced here. A question-answer format is used throughout, with major results enumerated in Key Points 1.1-1.5.

In 1996 and 2007,^{9–11} I suggested viewing entropy as a “spreading function.” Independently, chemist Frank Lambert^{12–15} proposed a similar idea. Stimulated by Lambert’s work, the energy spreading metaphor has been adopted by the authors of over two dozen general chemistry and physical chemistry textbooks. In contrast, the connection between energy spreading and entropy has not been widely embraced by authors of physics textbooks. This two-part article is an attempt to promote greater appreciation of the fact that entropy is in essence a spreading function.

Questions and answers

•What distinguishes thermodynamics from classical mechanics?

An inability to answer this question can make thermodynamics seem confusing. Classical mechanics deals with point particles and rigid bodies. Both of these are fictitious model systems that do not exist in nature, and are *not* thermodynamic systems. A point particle can neither rotate nor vibrate and thus cannot store energy within it. This differs from a real atom, which stores energy internally—energy that can vary by absorption and/or emission of radiation.

A rigid body’s atoms are assumed to be point-like, with fixed positions relative to one another, so energy cannot be added to or taken from such a model system. The simplicity of a rigid body makes it useful for approximating the behavior of real physical systems in classical mechanics, when changes in internal energy are negligible. In contrast, thermodynamics deals with systems that have internal degrees of freedom. For example, the molecules of a gas have kinetic energies and interact with one another via mutual potential energies. Figure 1

depicts (a) a hypothetical rigid solid with zero internal energy, $U = 0$ and (b) a dilute gas whose internal energy $U > 0$ and is variable.

In a macroscopic system the number of individual kinetic and potential energy terms is enormous and impossible to deal with individually. The many molecules of solids typically vibrate about localized lattice sites and have numerous translational, rotational, and vibrational energy modes. Similarly the prodigious number of molecules in a gas have kinetic and intermolecular potential energies. Recognizing the impossibility of dealing with these systems microscopically, the macroscopic internal energy function U is postulated in thermodynamics.

Key point 1.1: *The existence of internal energy that can be varied makes a system “thermodynamic.”*

• What is a “state function” and why is internal energy a state function?

A state function is what we normally call a *function* in mathematics. The internal energy function U , envisaged as an average total energy, is postulated to be a function of a small number of thermodynamic variables, e.g., temperature T , system volume V , and number N of molecules; i.e., for a given thermodynamic state, (T, V, N) , the internal energy $U = U(T, V, N)$. Typically, for systems with sufficiently short-range intermolecular forces, U is an increasing function of temperature T for fixed V and N .

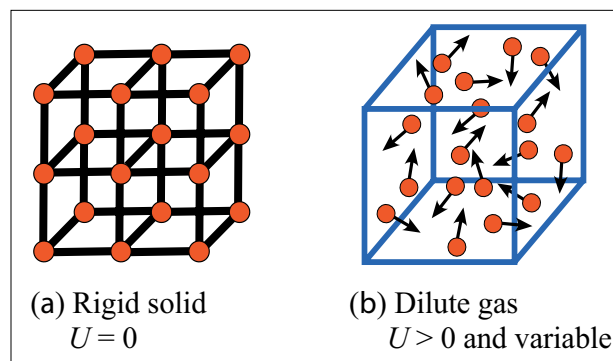


Fig. 1. Depictions of (a) a rigid solid, with zero internal degrees of freedom and zero internal energy, and (b) a dilute gas, whose internal energy consists primarily of the sum of all molecular kinetic energies. The model in (a) is *not* thermodynamic because its atoms are assumed to be point particles that are fixed relative to one another; i.e., there are no internal degrees of freedom and the internal energy is zero and unchangeable. The model in (b) represents a thermodynamic system with nonzero, variable internal energy.

Key point 1.2: State functions in thermodynamics describe equilibrium thermodynamic properties. They do not depend on how equilibrium was reached; i.e., they have no path or history dependence. Internal energy represents the energy stored within an object for a given thermodynamic state specified by a small number of thermodynamic variables such as (T , V , N).

• **Why are heat and work NOT state functions?**

It is important to understand that neither heat nor work is a function. Heat and work are best viewed as adjectives that indicate process types. Historically, however, the term *heat* was considered as either motion of *small particles*—even before the existence of atoms was established—or a conserved, stored entity referred to as heat or *caloric*.¹⁶ Largely because of remnants from the erroneous and obsolete caloric theory, the history of heat and the language used for it has been a tortuous one.¹⁷

In modern terms, a heat process is an energy *transfer* induced by a temperature difference, with the transferred energy denoted by Q . For example, heating water on a stove entails a temperature difference between burner and pot. A very different, but important, class of processes called *adiabatic* are *pure work* processes with $Q = 0$.

The simplest *work* process is an expansion or compression of a gas, induced by a pressure difference that results in the gas doing positive or negative work on its surroundings. We define W as the work done *by* the gas, so $W > 0$ when the gas expands, and $W < 0$ when the gas is compressed. With this convention, in an adiabatic volume change, if the work done is denoted by W_{ad} , then $\Delta U = -W_{ad}$. That is, in a slow adiabatic expansion, the gas does positive work, reducing its internal energy.

Generally, for a combination work plus heat process, we write the first law of thermodynamics as

$$\Delta U = Q - W. \quad (1)$$

Knowing the work W_{ad} for any adiabatic process that connects two equilibrium states determines $\Delta U = W_{ad}$. Then for any nonadiabatic process connecting the same two states, Q can be deduced by measuring W and using Eq. (1), $Q = \Delta U + W = W_{ad} + W$. This gives an operational definition of Q in terms of measurable work values for two different processes that connect two given states.

Suppose a gas is heated from state A to state B at constant pressure. It could instead be heated at constant volume from state A to an intermediate state C, with zero work, and then brought to state B by an adiabatic expansion. Because $\Delta U = U_B - U_A$ for both paths, AB and ACB, $Q_{AB} - W_{AB} = Q_{ACB} - W_{ACB}$, or equivalently, $Q_{AB} - Q_{ACB} = W_{AB} - W_{ACB}$. Path ACB entails higher pressures than AB, and thus $W_{ACB} > W_{AB}$ and $Q_{AB} > Q_{ACB}$.

The latter result is an example of the important point that rather generally, any two equilibrium thermodynamic states A and B can be connected by many different combined work

and heat processes. For example a process might entail segments with T , P , or V constant, each with different Q and W values. For each such combination, Q and W depend not only on A and B but on the specific path connecting them.

Key point 1.3: Heat and work are processes. The values of Q and W in $\Delta U = Q - W$ are dependent on the specific thermodynamic paths that connect equilibrium states, but notably, ΔU is the same for all paths. It is important to understand that Q and W are transient process energies and are not stored. Once a process is over, the system stores internal energy U , and there is no memory of Q or W , or the particular heat and/or work paths.

• **What is entropy and why does it occur in thermodynamics and not in mechanics?**

Entropy can be viewed usefully in terms of its changes during thermodynamic processes, which generally entail spatial redistributions of *internal* energy. As such, entropy has significance only for systems that store *internal energy*. Because neither a point particle nor a rigid body, the two mainstays of classical mechanics, stores internal energy, their entropy values are zero and unchanging. Thus, entropy is normally not even mentioned in classical mechanics. In contrast, macroscopic gases, liquids, and solids have internal degrees of freedom and store internal energies that can be varied by work and/or heat processes. Even an ideal gas, though composed of point particles, has internal energy because those particles have kinetic energy.

In a real thermodynamic process, an internal energy redistribution occurs and entropy is generated in the universe. For example, when a hot cup of soup cools, heating its surroundings slightly, energy spreads from the cup and soup to the surroundings until there is a uniform temperature. Were spreading to continue further, the soup would become cooler than the surroundings, which obviously does not happen! In this sense, energy spreads maximally—i.e., as much as is needed to generate temperature equality between soup, cup, and surroundings. The central idea of energy spreading maximally is the essence of the second law of thermodynamics. This is discussed in detail in Parts II-V of this series.

If two identical solid copper blocks at different temperatures are put in thermal contact, energy spreads as much as possible, becoming distributed equitably, namely uniformly, with each block having half the energy. Because different materials store internal energy differently, when equal masses of two different materials have equal temperatures, their internal energies differ in general, and the meaning of an equitable energy distribution is less evident *a priori*. This is addressed in Part V of this series.

Although it is possible for energy to “unspread” spatially, clumping in finite spatial regions, this happens only in special cases, and is accompanied by compensating redistributions of energy.¹⁸

Key point 1.4: Thermodynamic processes entail spatial redistributions of internal energies, namely, the spatial spreading of energy. Thermal equilibrium is reached when energy has spread maximally; i.e., energy is distributed equitably and entropy is maximized. Thus, entropy can be viewed as a spreading function, with its symbol S standing for spreading. Although not Clausius' motivation for using S , this can serve as a mnemonic device. Energy spreading can entail energy exchanges among molecules, electromagnetic radiation, neutrinos, and the like.

• **How is entropy calculated?**

Though it is often overlooked, every macroscopic material in thermodynamic equilibrium has a numerical entropy value that depends on its temperature, pressure, and possibly other variables, and these are tabulated in handbooks and on the Internet. Clausius' algorithm,

$$dS = \frac{dQ_{\text{rev}}}{T}, \quad (2)$$

enables calculation of entropy changes, namely, for a slow, reversible heating process,¹⁹ where infinitesimal energy dQ_{rev} is transferred to the system. We use the notation dQ_{rev} rather than dQ to remind us that Q_{rev} is not a state function and thus dQ_{rev} is not an "exact" differential; i.e. $\int_a^b dQ \neq Q_b - Q_a$. Indeed there exist no functions Q_a and Q_b .

The term *algorithm* is appropriate because Eq. (2) is a calculation tool that requires a *fictitious, reversible* process rather than the actual irreversible process (in Part IV, we explain that all real processes are irreversible). Given initial and final equilibrium states, any reversible path suffices. If the energy transfer is *from* the system, then $dQ_{\text{rev}} < 0$. The generalization of Eq. (2) for an irreversible process is $dS > dQ/T$,²⁰ where dQ is for the *actual* process. For example, an infinitesimal adiabatic free expansion, with $dQ = 0$, has $dS > 0$.

When a system is heated *very slowly* and *reversibly* at constant atmospheric pressure P , the added energy for each added tiny increment is $dQ_{\text{rev}} \equiv C_P(T) dT$, which defines $C_P(T)$, the heat capacity at constant pressure. (At constant volume, $dQ_{\text{rev}} \equiv C_V(T) dT$.) If heating is from initial temperature T_i to final temperature T_f , the constant-pressure entropy change is

$$\Delta S = \int_{T_i}^{T_f} \frac{C_P(T)}{T} dT. \quad (3)$$

Available data for C_P for solids at atmospheric pressure as a function of temperature enables numerical evaluation of ΔS . One can also calculate the enthalpy change,²¹ $\Delta H \equiv \int_{T_i}^{T_f} C_P(T) dT$, for many real solids using the lowest achievable minimum temperature $T_i \approx 0$ K and $T_f = 298.15$ K (a common reference temperature). For $T_i \rightarrow 0$, a simplification occurs using the third law of thermodynamics, namely, the zero temperature limit of entropy is zero for all pressures P . Thus $\Delta S = S(298.15) - 0 \equiv S^\circ$, the so-called *standard* entropy. Numerical values obtained using this procedure for solids will be presented in Part II.²²

Key Point 1.5: Heat capacity data for a solid from near absolute zero to 298.15 K at atmospheric pressure enables a numerical evaluation of standard entropy. Because all non-zero entropy values entail adding energy to a substance, it is clear that entropy and energy are intimately related. If the substance is a liquid or gas at 298.15 K and standard pressure, the entropy calculation is slightly more complicated, entailing a knowledge also of the so-called latent heat of melting and (for a gas) vaporization.

In Parts II-V of this series,²² we discuss the Clausius and Boltzmann entropies, numerical entropy, connections with stored internal energy, entropy's spreading nature, and its relationship with uncertainty. We show that entropy can be viewed with simple graphs, and is related to reversibility, irreversibility, constant-temperature reservoirs and the concept of equity.

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18. Clumping can occur in various ways. One example of clumping is the gas-liquid phase transformation for which clumping of particles in the liquid is accompanied by energy spreading to the surroundings, which preserves the second law of thermodynamics. Another example occurs in outer space, where long-range gravitational forces dominate. The formation of galaxies and stars entails clumping, along with continual spatial energy redistribution of kinetic and gravitational energy, electromagnetic radiation and neutrinos, which spread widely. The second law of thermodynamics is believed to be satisfied.
19. Reversible processes are discussed in depth in Part IV.
20. This inequality is useful only if T is well defined, which is not so for some irreversible processes. A more rigorous expression is $dS \geq dQ/T_{res}$, where T_{res} is the temperature of an (assumed) constant-temperature environment supplying the energy dQ . The equality holds only in the limit $T_{res} \rightarrow T$ and $dQ \rightarrow dQ_{rev}$. Constant-temperature reservoirs and reversible and irreversible processes are discussed further in Part III and IV of this article.
21. Enthalpy H is defined by $H = U + PV$, so $dH = dU + PdV + VdP$. From the first law of thermodynamics, $dU = dQ - dW$, and for a sufficiently slow and reversible process $dW = PdV$. Thus, $dH = dQ + VdP$, and for a constant pressure process, $dH = dQ \equiv C_p(T)dT$.
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