

About this document. This is a set of notes I have compiled while studying thermodynamics and statistical mechanics. Typing up these notes with the intention of presentation to an audience (that is, you) forces me to think more deeply about the material; none of the material will be new or original, though my presentation might allow a different perspective. Many statements, and particularly definitions, may be quoted verbatim without an explicit citation. Longer paragraphs are usually cited. The current books and papers I have used in creating this document are:

- ☞ Callen's *Thermodynamics and an Introduction to Thermostatistics*, second ed. A unique book that highlights the fundamental concepts and ideas behind thermodynamics. Chapter 21, on symmetry, is especially worth reading, as are all the chapters in Part I. I enjoyed the beginning chapters regarding statistical mechanics also.
- ☞ Chaikin and Lubensky's *Principles of Condensed Matter Physics*, first ed. A unique book on soft condensed-matter physics requiring an advanced physical and mathematical background. Despite the clear presentation of concepts, intuition, and mathematical formalism in this book, it remained very difficult to understand for me. Facility with Fourier transforms and functional differentiation is useful; the mathematical appendices are quite terse, and I would not have been able to follow the derivations had this been my first exposure to these mathematical techniques.

In addition, some papers are relevant but have yet to make it into these notes:

- ☞ ter Haar's *Foundations of statistical mechanics*, Rev. Modern Physics, 27, 3, 1955. Discusses in detail the ergodic hypothesis and theorem, including Boltzmann's H-theorem, in the classical and quantum-mechanical regimes.
- ☞ Jaynes's *Information theory and statistical mechanics*, Phys. Rev., 106, 4, 1957. Proposes using statistical inference and information theory, rather than physical principles, to justify statistical mechanics. This produces a clean split between the physical aspects of statistical mechanics—providing a “correct enumeration of the states of a physical system and their properties”—and the statistical aspects, which involve using statistical inference to make predictions. The information-theoretic perspective is very clean, but I am loath to give up my physical principles.
- ☞ van Kampen's *Quantum statistics of irreversible processes*, Physica, 20, 1954. I refer only to a small section of this paper, where van Kampen claims that isolated quantum systems have the same probability of being in each state *even if detailed balance does not hold*. I do not understand his proof.

§1. INTRODUCTION.

Callen, Introduction.

Thermodynamics is quite different [from mechanics and electromagnetic theory]. It neither claims a unique domain of systems over which it asserts primacy, nor does it introduce a new fundamental law analogous to Newton's or Maxwell's equations. In contrast to the specificity of mechanics and electromagnetism, the hallmark of thermodynamics is generality. Generality first in the sense that thermodynamics applies to all types of systems in macroscopic aggregation, and second in the sense that thermodynamics does not predict specific numerical values for observable quantities. Instead, thermodynamics sets limits (*inequalities*) on permissible physical processes, and it establishes relationships among apparently unrelated properties.

[... Whereas thermodynamics is not based on a new and particular law of nature, it instead reflects a commonality or universal feature of all laws. In brief, thermodynamics is the study of the restrictions on the possible properties of matter that follow from the symmetry properties of the fundamental laws of physics. (Callen, pp. 2-3)]

We will begin with a macroscopic treatment of thermodynamics, supported by an underlying microscopic picture. The microscopic viewpoint allows for a natural transition into statistical mechanics proper. Finally, we close the circle by applying the ideas of macroscopic thermodynamics to microscopic stochastic trajectories.

§2. MACROSCOPIC MEASUREMENTS. THERMODYNAMIC VARIABLES.

Callen, Ch. 1.1–1.2, Ch. 21.3–21.7; Chaikin and Lubensky, Ch. 8.1.

A macroscopic measurement coarse-grains the dynamics of a microscopic system over macroscopic length and time scales. Most microscopic variables will be annihilated by this procedure; only a select few, possessing some special symmetry, survive as macroscopic thermodynamic variables. These symmetries include:

- ☞ the discrete translational symmetry of a crystal lattice. Forming such a lattice breaks the continuous translational symmetry of a fluid; by Goldstone's theorem, a zero-frequency vibrational mode exists with infinite wavelength. This mode is associated with the volume of a crystal. Similar continuous-symmetry breaking accounts for the modes associated with the electric and magnetic dipole moments.
- ☞ the conservation law for particle densities. Assuming a linear constitutive relationship between the particle current and the gradient of the particle density, as with Fick's law, yields a diffusive dispersion relation between the mode frequency and the wavenumber; hence again a zero-frequency mode exists with infinite wavelength. This mode is associated with the volume of a fluid.
- ☞ the conservation of particle number, resulting from a gauge symmetry of particle physics. This mode is associated with mole numbers.
- ☞ time-translation symmetry, in the sense that the system's evolution is independent of the origin of time. By Noether's theorem, this mode is associated with the internal energy.

2.1 NORMAL MODES.

Definition. *Normal modes* (or *Fourier modes*, or simply *modes*) form the plane-wave eigenbasis of a physical system. Normal modes refer to plane waves oscillating in time, whereas Fourier modes may refer to oscillations in space or in time, depending on whether the Fourier transform considered is spatial ($\mathbf{x} \leftrightarrow \mathbf{k}$) or temporal ($t \leftrightarrow \omega$). These plane waves are respectively characterized by the wavevector \mathbf{k} and the frequency ω , and related by the *dispersion relation* $\omega = \omega(\mathbf{k})$. The *normal mode coordinates* are the coefficients of the system in this eigenbasis and represent the amplitude of each wave.

2.2 EXERCISES.

1. Demonstrate the diffusive dispersion relation associated with the particle density n and particle current \mathbf{j} given the conservation law and constitutive relationship

$$\frac{\partial n}{\partial t} = -\nabla \cdot \mathbf{j}, \quad \mathbf{j} = -\kappa \nabla n,$$

where κ is some constant of proportionality.

Solution. Eliminating \mathbf{j} yields the governing equation $\partial_t n = \kappa \nabla^2 n$. The dispersion relation is an equation in \mathbf{k} and ω , suggesting a Fourier transform in time and space, with

$$n(x, t) = \int d\mathbf{k} \int d\omega \tilde{n}(\mathbf{k}, \omega) e^{i\mathbf{k} \cdot \mathbf{x}} e^{-i\omega t}.$$

Substituting the Fourier transform into the governing equation gives

$$0 = \int d\mathbf{k} \int d\omega \tilde{n}(\mathbf{k}, \omega) e^{i\mathbf{k} \cdot \mathbf{x}} e^{-i\omega t} (\omega - i\kappa k^2).$$

Because the Fourier coefficients $\tilde{n}(\mathbf{k}, \omega)$ are independent by construction, $\omega - i\kappa k^2$ must vanish identically for this equation to hold; our desired dispersion relation is thus $\omega = i\kappa k^2$.

- ☞ This dispersion relation is diffusive in the sense that the governing equation is that for diffusion.
 - ☞ We integrate over ω and \mathbf{k} as independent variables, though we find that they are related *via* our derived dispersion relation. Is this valid? *Yes.* While the governing equation is satisfied only for $\omega = \omega(\mathbf{k})$, *i.e.*, for a curve in ω, \mathbf{k} -space, the Fourier transform acts on the whole space, not the constrained curve, and in this space \mathbf{k} and ω are indeed independent.
2. One-dimensional elastic systems, like rubber bands, have length as a thermodynamic variable. Describe the symmetry that allows such an identification.

Solution. Of the four types of symmetries stated, only the first two are general, so we expect this to be either a continuous-symmetry breaking or a conservation law. The atoms in a rubber band are not able to move freely—strong cross-linking prevents the relative movement of atoms—and so the linear constitutive relationship between particle current and gradient of particle density does not hold in general. We can think of an unstretched rubber band as consisting of coiled polymeric chains, each segment of which may be oriented randomly. When stretched, these polymeric chains straighten out, and we break continuous rotational symmetry in the chain. By Goldstone's theorem, this results in a zero-frequency mode associated with length.

§3. THE COMPOSITION OF THERMODYNAMIC SYSTEMS. EQUILIBRIUM.

Callen, Ch. 1.3–1.5.

We restrict our study to *simple systems*, which are macroscopically homogeneous, isotropic, and uncharged, large enough that surface effects may be neglected, and with no applied electric, magnetic, or gravitational fields. If necessary, we may reinstate the possibly complicated mechanical and electrical properties of these systems, thereby introducing shear, mass, and electric and magnetic dipole moments in our description, but the thermodynamic framework will remain unchanged.

Simple systems are characterized by macroscopic thermodynamic variables like the internal energy U , volume V and the mole numbers N_i corresponding to each species i in the system. To be concise, we will let N denote all of the mole numbers N_i . In general, these variables are insufficient for complete characterization of the system, which may be dependent on its past states.

- ☞ In two-dimensional and one-dimensional systems, such as a bubble and a rubber band respectively, the surface area A and the length L replace the volume V as the relevant thermodynamic variable.

Example. Drip an inkdrop into a glass of water. The internal energy, volume, and mole numbers of each species in the glass remain constant, but the system clearly evolves in time as the ink diffuses into the water, *i.e.*, the state of the system depends on when the inkdrop was introduced into the system. However, the system eventually reaches a time-independent state, where the inkdrop has diffused homogeneously throughout the glass of water.

Definition. An *equilibrium state* is a time-independent state of a system upon which there is no external influence. In particular, such states cannot depend on the history of the system.

- ☞ Time-independent states upon which there *is* external influence are known as *steady states*. Here, external forces are actively applied to keep the system in a time-independent state.
- ☞ Convergence to equilibrium may be fast or slow. If convergence occurs on much slower a timescale than that for experimental analysis (a *separation of timescales*), then the system exists in *metastable equilibrium*, and our thermodynamic framework applies.

Postulate I. Equilibrium states of simple systems exist and are completely characterized at a macroscopic level by the extensive variables U , V , and N .

Extensive variables are discussed in the following section.

§4. EXTENSIVITY AND INTENSIVITY. SURFACE EFFECTS AND LONG-RANGED FORCES.

Definition. An *extensive* variable scales linearly with the size of the system. An *intensive* variable does not scale with the size of the system.

Example. V and N are extensive variables. U is extensive for a simple system, but may not be in general. Extensivity of U is precluded by surface effects and long-ranged forces, both of which are dealt with by the definition of a simple system.

- ☞ Consider two identical systems placed side by side, each with energy U' . The energy of the composite system is $2U' + U_{\text{int}}$, where U_{int} denotes the interaction energy between the two systems. When the two systems interact *via* short-ranged forces, their interaction is a localized surface phenomenon that scales as one lower dimension than does the system, and is negligible for large system size. When the two systems interact *via* long-ranged forces, however, their interaction is no longer localized and cannot be neglected; we must therefore exclude long-ranged forces from consideration.
- ☞ *Long-ranged forces* scale with distance as r^{-d} or faster, where d is the dimensionality of the system. These forces are long ranged in the sense that the total interaction energy for an infinitely large system diverges: for the limiting case of an inverse-cube force law in three dimensions, we have

$$F(r) \sim r^{-3} \implies U_{\text{int}} \sim \int d\mathbf{r} F(r) \sim \int dr r^2 F(r) \sim \int dr r^{-1} \sim \infty,$$

where \sim denotes proportionality. The interaction energy diverges logarithmically for a force law scaling as r^{-3} or faster, but converges for any scaling slower than r^{-3} .

- ☞ In three dimensions, the common inverse-square force laws associated with gravity and electromagnetism are long-ranged forces. Macroscopic charge neutrality prevents the existence of charge monopoles in a system; the most significant electrostatic interactions are dipole-dipole interactions, with a force law scaling as r^{-4} , and we are safe. There is no corresponding mass neutrality for gravity, but the relative weakness of the gravitational force allows for its neglect in most situations.

Example. The pressure p , temperature T , and chemical potential μ , which have yet to be formally introduced, are intensive variables.

Example. Let $f(x, y, z)$ be an extensive function depending on the extensive variables x and y and the intensive variable z . Let λ denote a scale factor for the system. Then $\lambda f(x, y, z) = f(\lambda x, \lambda y, z)$.

Theorem. (Euler's homogeneous function theorem.) Let f be defined as in the previous example. Then

$$f(x, y, z) = x \frac{\partial f}{\partial x} + y \frac{\partial f}{\partial y}.$$

Proof. Differentiate the identity $\lambda f(x, y, z) = f(\lambda x, \lambda y, z)$ with respect to λ , then set $\lambda = 1$.

4.1 EXERCISES.

1. Where is the mistake in this argument?

Consider a volume V of water and the same volume V of ethanol. When the two liquids are combined, the resulting solution has volume $2V' < 2V$. Therefore, volume is not an extensive variable.

Solution. The original subsystems—a volume V of water and a volume V of ethanol—are not the same, so extensivity does not apply. On the other hand, if we had started out with a volume V' of equivolometric amounts of water and ethanol and added to it the same volume V' of such a mixture, then the resulting solution *must* have volume $2V'$ by extensivity.

2. Consider three thermodynamic variables x , y , and z . Upon scaling the system by a scale factor λ , the variables transform as $x \rightarrow \lambda x$, $y \rightarrow y$, and $z \rightarrow z/\lambda$. Identify the following quantities as extensive, intensive, neither, or variable: x , y , z , xy , xz , yz , 1 , x^2 , y^2 , z^2 , x^{-1} , y^{-1} , z^{-1} , $x + y$, $xz + y$, $\ln y$, e^y , αx , βy , $f(x)$, $g(y)$, xy^{-1} , $\partial x/\partial y$, $\partial y/\partial z$, $\alpha x + \beta z^{-1}$. α and β are arbitrary constants. f and g are arbitrary functions. Where partial derivatives appear, assume that they are non-zero.

Answer. Extensive. Intensive. Neither. Extensive. Intensive. Neither. Intensive. Neither. Intensive. Neither. Neither. Intensive. Extensive. Neither. Intensive. Intensive. Intensive. Extensive. Intensive. Variable. Intensive. Extensive. Extensive. Extensive. Extensive.

3. Let $g(x, y, z)$ be an intensive function depending on the extensive variables x and y and the intensive variable z . Let λ denote a scale factor for the system. Identify $g(\lambda x, \lambda y, z)$, and hence show that $g(x, y, z) = g(x/y, z)$. In general, an intensive function of $n \geq 2$ extensive variables and m intensive variables can instead be written as a function of $n - 1$ intensive variables along with the original m intensive variables.

Solution. We have $g(\lambda x, \lambda y, z) = g(x, y, z)$ by intensivity. Taking $\lambda = y^{-1}$ yields the desired equality.

§5. THE CENTRAL PROBLEM OF THERMODYNAMICS. THE ENTROPIC POSTULATES.

Callen, Ch. 1.9–1.10. I use the term *isolated* where Callen uses *closed*.

The central problem of thermodynamics is to determine the equilibrium state that results after removing the internal constraints in an isolated composite system.

Definition. A *composite system* is composed of multiple simple systems.

Definition. *Internal constraints* prevent or restrict the flow of energy, volume, or matter among the simple systems constituting the composite system.

Definition. An *isolated* system cannot exchange energy, volume, or particles with its surroundings.

Example. The universe is an isolated system.

- An isolated composite system is thus quite general: let one system be the system of interest, and another system be everything else in the universe (the *surroundings*). Their composition is the universe, which is isolated.

For convenience, we restate Postulate I here.

Postulate I. Equilibrium states of simple systems exist and are completely characterized at a macroscopic level by the extensive variables U , V , and N .

- ☞ This postulate provides a means of identifying equilibrium states: a system is in an equilibrium state if its properties are consistently described by thermodynamics. Otherwise, the system must be out of equilibrium.
- ☞ Such an inconsistency in the heat capacity of H_2 allowed for the discovery of *ortho*- and *para*-hydrogen. The proton that makes up the nucleus of atomic hydrogen is a spin-1/2 fermion, and the coupling of atomic nuclei in H_2 may lead either to the triplet (spin-1) state of *ortho*-hydrogen or the singlet (spin-0) state of *para*-hydrogen. These states have different properties and lead to a heat capacity that differs significantly from that predicted for “regular” hydrogen. We re-visit this problem in [XX], where we perform the relevant statistical-mechanical calculations for each of these cases.

Postulate II. There exists a function—the entropy S —of the extensive parameters of any composite system defined for all equilibrium states. The values assumed by the extensive parameters in the absence of an internal constraint are those that maximize the entropy over all constrained equilibrium states.

- ☞ The entropy is not defined for non-equilibrium states.
- ☞ Any system can be thought of as a composite system by the introduction of suitable, possibly imaginary, constraints whose effects vanish at equilibrium, so the definition of entropy can be extended to all systems.

Definition. The relation that gives the entropy as a function of the extensive parameters is known as the *fundamental relation*.

- ☞ This relation is fundamental in the sense that it solves the fundamental problem of thermodynamics, because the equilibrium state can then be determined by extremizing the entropy with respect to these parameters. In other words, this relation contains all thermodynamic information about the system.

Postulate III. The entropy of a composite system is additive over the constituent subsystems. The entropy is differentiable—hence continuous—and is a monotonically increasing function of the energy.

- ☞ As a corollary, the entropy is extensive. Extensivity is the restriction of additivity to similar systems, in which the U , V , and N of one system are linearly proportional to those of another.
- ☞ If the entropy is differentiable and monotonically increasing with energy, then so too is the energy differentiable and monotonically increasing with entropy by the inverse function theorem. This allows for the representation $U = U(S, V, N)$ from $S = S(U, V, N)$.

Postulate IV. The entropy of any system vanishes in the state at which $(\partial U/\partial S)_{V,N} = 0$.

- ☞ We will later identify $(\partial U/\partial S)_{V,N} = T$; that is, this postulate states that the entropy of any system vanishes at zero temperature.
- ☞ This postulate is known also as the Nernst postulate or as the third law of thermodynamics. It is inessential to the central development of thermodynamics, and we return to it in [XX].

The fundamental justification for these postulates, and all physical postulates in general, is agreement with empirical data. This is true in particular for Postulates I and IV. Postulate II can be understood further from the microscopic perspective of statistical mechanics, which we leave to [XX]; and Postulate III lists the simplest self-consistent set of mathematical properties that is convenient for entropy to have.

- ☞ For example, the transformation $S = S(U, V, N)$ to $U = U(S, V, N)$ is particularly useful, and for this transformation to be well-defined in general requires that S be differentiable and monotonically increasing with respect to U ; hence we postulate exactly these properties for S .

5.1 EXERCISES.

1. Where is the mistake in this argument?

Postulate III implies that the entropy is concave. Consider two systems sharing the fundamental relation $S = S(U, V, N)$ but with different values of the extensive parameters U , V , and N . To avoid clutter, we denote $S(U, V, N)$ as $S(\mathbf{M})$. Join a fraction $1 - \lambda$ of the first system with a fraction λ of the second system to form a composite system. When this system reaches equilibrium, by additivity and Postulate II, it has entropy

$$S((1 - \lambda)\mathbf{M}_1 + \lambda\mathbf{M}_2) \geq (1 - \lambda)S(\mathbf{M}_1) + \lambda S(\mathbf{M}_2).$$

This inequality, which holds for arbitrary choices of the original subsystems, defines concavity.

Solution. While S may be additive, V is not additive in general, so the volume of the composite system is not necessarily the sum of the volumes of the subsystems. For a concrete example, see the exercises in §4. When chemical reactions are involved, N also fails to be additive. On the other hand, U is indeed additive for simple systems, following the arguments in §4 and using conservation of energy, discussed further in the next section.

- ☞ Additivity generalizes extensivity: parameters—like U —that are additive must be extensive, whereas parameters—like V and N —that are extensive need not be additive.
- ☞ The incorrect argument made in the exercises of §4 may be corrected by simply replacing ‘extensive’ with ‘additive’.

2. Identify which of the following are acceptable fundamental equations given the entropic postulates. Ignore unit mismatches; unimportant constants have been omitted. $S = (NVU)^{1/3}$, $S = (NU/V)^{2/3}$, $S = (NU + V^2)^{1/2}$, $S = V^3/NU$, $S = (N^2VU^2)^{1/5}$, $S = N \ln(UV/N^2)$, $S = (NU)^{1/2} \exp(-V^2/N^2)$, $S = (NU)^{1/2} \exp(-UV/N)$, $U = S^2/V \exp(S/N)$, $U = NV(1 + S/N) \exp(-S/N)$. (Callen, 1.10-1)

Solution. We perform three passes through each equation, checking first for extensivity, then monotonicity, then the zero-temperature behavior, based on which property is easiest to check. We identify unacceptable fundamental equations by the first property they do not satisfy.

Acceptable. Not extensive. Acceptable. Not monotonically increasing. Acceptable. Entropy not zero at zero temperature. Acceptable. Not monotonically increasing. Acceptable. Not extensive.

- ☞ While Postulate III claims the stronger property of additivity, we cannot check this property because there is no information provided regarding subsystems.

§6. HEAT AND WORK. THE FIRST LAW OF THERMODYNAMICS.

Callen, Ch. 1.2.

Definition. A macroscopic description of a system is obtained by coarse-graining over its microscopic modes. Some of these modes have symmetries that allow them to manifest even in a macroscopic system; energy transferred by these modes is *work*. Energy transferred by the hidden microscopic modes is *heat*.

Energy is conserved. It is defined by its conservation law, the first law of thermodynamics:

$$dU = dq + \mathfrak{d}w.$$

In words, any (infinitesimal) change in the energy of the system is the result of a corresponding (infinitesimal) transfer of heat q or work w into or out of the system.

- ☞ We use \mathfrak{d} to denote an *inexact differential*, which is path-dependent, as opposed to an *exact differential*, which is not. A path is required to specify the value of a quantity with an inexact differential.

- Consider two systems characterized by the thermodynamic variables (U_1, V_1, N_1) and (U_2, V_2, N_2) respectively. Heat and work are path-dependent in the sense that different paths linking the two systems on a thermodynamic state space—the hyperspace defined by the relevant thermodynamic variables for the system, here the three-dimensional space spanned by U , V , and N —may lead to a different value of heat or work transferred. In other words, the heat or work required to go from (U_1, V_1, N_1) to (U_2, V_2, N_2) is not specified until a path between the two states is chosen.