

# Notes on Thermodynamics and Statistical Physics

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# 1 Questions and Ideas

## Books to Read

- Perhaps Kolmogorov: Ergodic Motion
- The Logic of Thermostatistical Physics: QC311.5 .E63 2002

## What About?

- (Reif Ch 15) Irreversible processes and Fluctuations, magnetic resonance, Brownian motion and the Langevin equation, Nyquist's theorem, Onsager relations
- Law of mass action
- ...

## Questions

- One of the major confusions seems to be that functions of different variables are written with the same symbol. For example,  $\bar{N} = \bar{N}(T, P)$  and  $\bar{N} = \bar{N}(\mu, ?)$   
Can we fix this problem?
- Does temperature mean average energy per  $k$  per degree of freedom? (cf. Equipartition Theorem)
- Does entropy mean the number of degrees of freedom, or "heat" degrees of freedom, or something else? When  $dS = \bar{d}Q/T$ ,  $\bar{d}Q$  is the change in energy due to heat (or change in heat energy, if one can say that), and  $T$  could be proportional to the energy per degree of freedom.
- Does chemical potential mean average energy per particle? or per interaction between particles?
- If a usual mercury-filled thermometer is placed in a vacuum, what should it read? (I guess it should read whatever it read before it was placed in the vacuum, but slowly mercury vapor and atoms may leak out.)
- If a person (37 °C) is placed in a very dilute gas that is at (37 °C), that person will not remain at the same temperature, since it will transpire or transpire, losing heat, and perhaps explode. Right?

# 2 The Big Picture

Thermodynamics is concerned with the relationship between thermal, mechanical, and chemical (and perhaps electromagnetic) interactions and equilibria (and small fluctuations about equilibria?) on a macroscopic scale. It describes macroscopic behavior of systems but does not always describe mechanisms behind that behavior. (Does statistical physics always describe mechanisms? I don't think so...)

Define: kinetics and statistical physics proper (statistical mechanics, "statistical thermodynamics" (Reif pg 124))

Various approaches to thermodynamics: macroscopic/historical, (modern) micro-statistical, (macroscopic?) variational (Callen's approach, postulating the maximization of some state function  $S$ )

Callen says that "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." (This statement seems to link thermodynamics with statistical physics and modernize the term.)

From <http://www.jgsee.kmutt.ac.th/exell/Thermo/Systems.html>, Thermodynamics:

The theory is restricted to closed thermodynamic systems. A closed thermodynamic system is a quantity of matter separated from its environment by a container. The system has a set of equilibrium states. These equilibrium states are the basic elements of the theory.

A transition is a change from one equilibrium state to another. The theory is about what transitions are possible and what energy exchanges occur between the system and its environment during transitions. During a transition a system may pass through non-equilibrium states. In such cases the theory deals only with the relation between the end states and with the total effect of the transition; it cannot deal with the non-equilibrium states between the end states.

## Domains

- Deterministic versus Statistical (or Analytic versus Statistical)
- Microscopic versus Macroscopic
- Thermodynamic limit (number of particles/atoms/molecules  $\rightarrow \infty$ , or  $\gtrsim$  Avogadro's number)
  - manipulating factorials arising from Boltzmann's formula for the entropy,  $S = k \log W$ , by using Stirling's approximation, which is justified only when applied to large numbers.
  - In some simple cases, and at thermodynamic equilibrium, the results can be shown to be a consequence of the additivity property of independent random variables; namely that the variance of the sum is equal to the sum of the variances of the independent variables. In these cases, the physics of such systems close to the thermodynamic limit is governed by the central limit theorem in probability.
  - Fluctuations become negligible for most quantities (except for scattering of light, or near the critical point, or in electronics with shot noise and Johnson-Nyquist noise, or near absolute zero with Bose-Einstein condensation, superconductivity and superfluidity.)
  - It is at the thermodynamic limit that the additivity property of macroscopic extensive variables is obeyed. That is, the entropy of two systems or objects taken together (in addition to their energy and volume) is the sum of the two separate values.
- Non-relativistic, Relativistic, and Super-relativistic
- Classical versus (Quantum or something else...since quantum systems are sometimes described as classical or semi-classical)
  - One obtains in the classical approx.  $Z = \int \dots \int e^{-\beta E(q_1, \dots, p_f)} \frac{dq_1 \dots dp_f}{h_0^f}$  (Reif pg 238)

## Historical Development of Theory

Can I break Thermo into a set of theories? (Particle/Atomic Theory of Matter or "Quantum" Theory of Matter or "Quantum" Theory of "Wavicles" or "Quanta", Kinetic Theory of Heat, Blah-blah Theory of Energy (and/or Energy Exchange), Conservation of Energy, ...)

- **Phlogiston Theory** (~1669 – )
  - The Idea:
  - Creators: J.J. Becher, Georg Ernst Stahl: theory of combustion involving combustible earth, or phlogiston
  -
- **Caloric Theory** (~1783 – )
  - The Idea:
  - 1783 - Antoine Lavoisier deprecates the phlogiston theory and proposes a caloric theory
  - Proponents: John Dalton, Sadi Carnot (analyzed engines using caloric theory), Émile Clapeyron
  - Detractors:

- **Kinetic Theory** (~1738 – present)
  - The Idea: (for certain domains)
  - 1620 - Francis Bacon suggests heat is related to motion
  - 1738 - Daniel Bernoulli initiates the kinetic theory
  - Count Rumford (Benjamin Thompson) measures the frictional heat generated in boring cannons, Robert Brown (Brownian motion)
  - 1842 - Julius Robert von Mayer calculates the mechanical equivalent of heat
  - 1843 - John James Waterston fully expounds the kinetic theory of gases, but is ridiculed and ignored
  - 1843 - James Joule experimentally finds the mechanical equivalent of heat
  - 1856 - August Krönig publishes an account of the kinetic theory of gases, probably after reading Waterston's work
  - 1857 - Clausius gives a modern and compelling account of the kinetic theory of gases in his *On the Nature of Motion Called Heat*
  - 1859 - James Clerk Maxwell discovers the distribution law of molecular velocities
  - 1905 - Einstein mathematically analyzes Brownian motion as a result of random molecular motion
  - 1916 - Sydney Chapman and David Enskog systematically develop the kinetic theory of gases.
  - 1919 - James Jeans discovers that the dynamical constants of motion determine the distribution function for a system of particles
- **Conservation of Energy, Entropy, Other Random Thermo Theory**
  - 1876 - Josiah Willard Gibbs publishes the first of two papers (the second appears in 1878) which discuss phase equilibria, statistical ensembles, the free energy as the driving force behind chemical reactions, and chemical thermodynamics in general.
  - 1927 - John von Neumann introduces the density matrix representation and establishes quantum statistical mechanics
  - 1929 - Lars Onsager derives the Onsager reciprocal relations
  - 1942 - Joseph Leo Doob states his theorem on Gauss-Markov processes
  - 1957 - Aleksandr Solomonovich Kompaneets derives his Compton scattering Fokker-Planck equation.
  - 1957 - Ryogo Kubo derives the first of the Green-Kubo relations for linear transport coefficients.

### 3 Notation and Conventions

The study of thermodynamics has revealed to me that physics is still developing its conventions and vocabulary. Some terms, such as *equation of state* and *fundamental relation* (or *fundamental equation*), do not seem to be used completely consistently among different sources. (Callen [1] seems to define these terms most clearly.) Also, some useful terms, such as *internal parameter* and *external parameter*, seem only to be used by some authors (Reif [2]) and then not even defined well. I will try to cite some sources for definitions, but I will also try to provide my best interpretation (and perhaps minor extension or honing) of them. Precise terms make for precise understanding and expression – anything else is maddening in a scientific context.

My notation differs from, but combines, Callen's and Reif's notations. For example, where Callen defines  $P_k \equiv \frac{\partial U}{\partial X_k}$  and Reif defines  $\bar{X}_k \equiv -\frac{\partial \bar{E}_T}{\partial x_k}$ , the mean generalized force conjugate to  $x_k$ , I define  $P_k \equiv -\frac{\partial E}{\partial X_k}$ , the (mean) generalized force conjugate to  $X_k$ .

I also try to be careful about distinguishing the total energy  $E$  from the internal energy  $U$ .

Context-dependent equalities: (Perhaps I'll use this...) In general, a quantity is not the same as its average (over (a local interval of) time and space). But occasionally, I will equate the two when it is appropriate and not mention that I am doing so. In those cases, it would be nice if I would give some indication that the equality is context-dependent: In general  $P_k \neq \bar{P}_k$ , but sometimes when it is true that  $P_k \approx \bar{P}_k$ , and  $\bar{P}_k$  is equal to some function  $f$ , I'll write  $P_k \stackrel{c}{=} f$ .

Possible ambiguities: Some quantities may be defined several different (consistent) ways. Some quantities may go by several different names. (There may be overlap in names for different quantities (magnetic field).) Some quantities do not have standardized definitions, names, or symbols. (Fermi energy?) Some quantities are commonly represented with the same symbols. ( $\mu$ ; chemical potential or Joule-Thompson coefficient.) Some quantities are often represented by several different symbols in different contexts. ("Occupancy"  $n_s, f(\epsilon)$ )

Less ambiguity: Other terms are much less ambiguous. ()

Name of Constant	Symbol	Value
Boltzmann constant	$k$ (oftentimes written elsewhere as $k$ or $k_B$ )	$1.38 \times 10^{-23}$ J/K
Electrostatic (Coulomb) constant	$K_e$ (oftentimes written elsewhere as $k$ or $k_C$ )	$8.99 \times 10^9$ Nm <sup>2</sup> /C <sup>2</sup>

- $\check{E}$  is a possible energy of a system given certain constraints. It may or may not be the equilibrium energy  $E$  ( $\langle E \rangle$  or  $\bar{E}$ ) or the instantaneous energy  $E(t)$  (at a given moment  $t$ ).

## 4 Mathematical Techniques

### Quantity Analysis

- Euler's Theorem for homogeneous functions (re: extensive variables, +fund. rel.  $\rightarrow$  Gibbs-Duhem rel.) (See Reif, footnote on pg 314)
- Method of Lagrange's undetermined multipliers
- Generalized forces and displacements (related here to multipliers?)

### Probability and Statistics

- Counting states...

### Approximations

- Taylor expansions, Maclaurin expansions
- (Virial expansion? coefficients?)
- Rapidly increasing function  $\rightarrow$  look at its logarithm, Taylor expand that
- Stirling's Approximation  
Similar to Method of Steepest Descent (...complex plane)  
Watson's Lemma  
Asymptotic (convergence?)
- Rapidly increasing function times rapidly decreasing function  $\rightarrow$  sharply peaked function

### Transformations

- Legendre transforms: Thermodynamic potentials and Massieu functions (rearranging complete sets of variables?)

General 1-D form:  $Y(X) \rightarrow \psi(P) = Y - PX \equiv Y[P]$  ( $= Y(X) - PX?$ ),  $P \equiv \frac{dY}{dX}$   
 What's the difference between a Legendre transform and taking a derivative?  
 How can you tell what the independent variables are?  
 $P \equiv dY/dX$ ,  $Y(X) \rightarrow U(P) = Y - PX = Y(X) - PX$  ???  
 $U(P, Y, X)$  ???  
 Compare to multidimensional forms.

- ...

## Partial Differential Equations

- Maxima, (Calculus of variations?) and the method of Lagrange multipliers ( $\rightarrow$  conjugate variables, maximizing energies and entropies?)
- Flipping derivatives, Jacobians, etc.
  - Given three variables  $x$ ,  $y$ , and  $z$ , two of which are independent, such that there are functional relationships  $z = z(x, y)$  and  $x = x(y, z)$ , then

$$\left(\frac{\partial x}{\partial y}\right)_z = -\frac{(\partial z/\partial y)_x}{(\partial z/\partial x)_y}$$

$$\left(\frac{\partial x}{\partial z}\right)_y = \frac{1}{(\partial z/\partial x)_y}$$

- See a case where “the partial derivatives  $[\partial x'/\partial x]$  and  $[\partial x/\partial x']$  are not the algebraic reciprocals of each other” here: <http://www.mathpages.com/home/kmath024/kmath024.htm>
- Bridgman's Thermodynamic equations (technique)

## 5 Terms

### 5.1 Overview

- Fundamental Thermodynamic Vocabulary
  - Systems and States
  - State Parameters and their relationships and constraints
  - Thermodynamic processes
  - Equilibria and the Fundamental Thermodynamic Postulate
- Thermodynamic Quantities
  - Energy, Work ( $\leftarrow$ ?chemical potential? $\rightarrow$ ) and Heat
  - Heat, Entropy, and Temperature
  - Auxiliary Energy and Entropy Functions
- Statistical Mechanics Terms
  - Number of States, Density of States
  - Probability density (functions) (e.g. “distribution function”)
  - Number of particles per state  $\rightarrow$  occupancy function
  - Mean value of a parameter
  - (5+) Statistical Ensembles

- Partition Functions, Boltzmann Factor
- (3+) “Statistics”, etc.
- Symbols Defined for Proofs, Comments on Terms, More Thermodynamic Quantities

## 5.2 Fundamental Thermodynamic Vocabulary

- **System** - A physical system is simply a set of physical objects, real or imagined. Systems and their constraints usually must be well-defined (using parameters) if precise statements are to be made about them. We consider properties and phenomena at different spatial scales: macroscopic and microscopic scales. Since we assume systems are made of atoms or particles, these scale distinctions are important. We also consider various temporal scales (e.g., time intervals required for thermal equilibration within or among systems, called “relaxation times”, or time intervals of experimental interest). (What about energy scales, etc?)
  - The complement of a physical system, i.e., all physical objects in the universe other than those in the system, is often called that system’s **environment**. Let’s define “environment” as such. (The word “environment” sometimes connotes “immediate environment”, but that is not what is meant here, so be careful.)
  - An **isolated system** is a system that does not interact with its environment; no external forces act upon it and no energy or matter is exchanged with its environment. (I should probably be careful about such strange phrases as energy “leaving, crossing boundaries, flowing” etc.)  
Constant total energy, an isolated system has.
  - A **thermally isolated** or **thermally insulated system** is a system that cannot interact thermally with its environment and can only interact mechanically. I.e., it may only interact via work, with changing external parameters, and not via heat, with changing internal parameters (Reif?).  
An **adiabatic** boundary, barrier, or envelope prevents heat flow, thermally isolating the system, and allows only adiabatic processes to occur.
  - A **mechanically isolated system** is a system that cannot interact mechanically (through macroscopic work) and can only interact thermally.  
(Constant “external” energy, a mechanically isolated system has?)
  - A **closed system** (or energetically closed system?) is a system that cannot exchange matter or internal energy with its environment, while there may be external forces (and change in total energy)... (see Callen pg 17,26)  
Constant internal energy, a closed system has.
  - A **materially closed system**<sup>1</sup> is a system in which no matter is exchanged with its environment. (There may be external forces and energy may be exchanged (in the form of heat or work, the only means of exchange by Reif’s definition).) (In the context of chemistry, this is often called simply a *closed system*.)  
(The mass of a materially closed system may change if there are nuclear reactions or particle decays, i.e., radioactivity.)
  - A **simple system** is defined by Callen as a system that is macroscopically homogeneous, isotropic, and uncharged, that is large enough so that surface effects can be neglected, and that is not acted on by electric, magnetic, or gravitational fields. (This type of system is most often the focus of thermodynamics texts.)

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<sup>1</sup>I haven’t seen this term yet.

- A **composite system** is a collection of simple systems. (From Callen page 26)
- Note: These terms imply the existence of the terms *thermally conducting (boundary)*, *(energetically) open*, and *materially open*.
- **State** - A state of a system is essentially a particular configuration of the qualities of that system. Scientists quantify these qualities and call them **state parameters**. There are several contexts in which to view the state of a system: microscopic, macroscopic, matter phase, etc. (Mechanical, Electromagnetic, Chemical, and Thermal States) The most fundamental context is the microscopic state, which implies all other types of states. (Aren't there degrees of microscopy? See below:)
  - (Quantum) Microscopic State: the configuration of quantum numbers of a system?
  - (Classical) Microscopic State: the configuration of positions and motions (velocities) of the constituent particles of a system. (What about excited-states for particles, nuclear states and decay, and the such?)
  - (Mechanical (or "Classical"??)) Macroscopic State: (deformation, chemical, electrical states?) the configuration of positions and motions (velocities) of the constituent macroscopic (rigid-body or effectively rigid-body...) pieces of a system.
  - (Thermodynamic) Macroscopic State:

### Macrostate versus Microstate

("microstate" may refer to a state of the whole system (or to the state of one particle?))

### Constraint - Accessible versus Inaccessible States

- **internal constraints** are constraints that prevent the flow of energy, volume, or matter among the simple systems constituting a composite system. (From Callen page 26)

**Phase** (as opposed to phase in "phase space")

- **Degree of Freedom** - ( $\simeq$ an axis in  $n$ -D phase space, where  $n$  is the number of degrees of freedom) The number of degrees of freedom of a system is the the minimal number of scalar quantities required to specify completely the state of that system [(which may be constrained in some manner) within a particular context].

The context may be macroscopic or microscopic

Depending on the type (what's a better word than "type" here) of state in question, the number of degrees of freedom may vary. (It may be that the number of degrees of freedom is more fundamental than the quantities that may count as a degree of freedom.)

(more parameters? or just more accessible states?) I think these are:

Definitions of *independent*: linearly, statistically, wrt energy function (more?)

- The set of degrees of freedom  $X_1, \dots, X_N$  of a system is independent if the energy associated with the set can be written in the following form:

$$E = \sum_{i=1}^N E_i(X_i), \text{ where } E_i \text{ is a function of the sole variable } X_i.$$

- \* If  $X_1, \dots, X_N$  is a set of independent degrees of freedom then, at thermodynamic equilibrium,  $X_1, \dots, X_N$  are all statistically independent from each other.

For  $i$  from 1 to  $N$ , the value of the  $i$ th degree of freedom  $X_i$  is distributed according to the Boltzmann distribution. Its probability density function is the following:

$$p_i(X_i) = \frac{e^{-\frac{E_i}{k_B T}}}{\int dX_i e^{-\frac{E_i}{k_B T}}}$$

- A degree of freedom  $X_i$  is quadratic if the energy terms associated to this degree of freedom can be written as:

$$E = \alpha_i X_i^2 + \beta_i X_i Y, \text{ where } Y \text{ is a linear combination of other quadratic degrees of freedom.}$$

– Derive equipartition theorem (somewhere).

Quadratic independent degrees of freedom and the equipartition theorem

– [http://en.wikipedia.org/wiki/Degrees\\_of\\_freedom\\_\(physics\\_and\\_chemistry\)](http://en.wikipedia.org/wiki/Degrees_of_freedom_(physics_and_chemistry))

(See “heat bath” in heat description)

“Consider a system of  $f$  degrees of freedom so that  $f$  quantum numbers are required to specify each of its possible states.” (Reif pg 61)

– **Phase Space** -

Volume in phase space:  $\delta p \delta q = h_0$

$\delta p_1 \delta q_1 \delta p_2 \delta q_2 \cdots \delta p_f \delta q_f = h_0^f$

$h_0$  has the same units as action (like Planck’s constant  $h$ ) and torque

• **Macroscopic, Microscopic Parameter** - A macroscopic parameter is a macroscopically measurable quantity that characterizes the macrostates of a system (such as  $V$ ,  $P$ , and  $E$ , although only  $\Delta E$  is truly measurable). A microscopic parameter characterizes microstates of the system’s particulate constituents. If there are  $f$  microscopic or macroscopic *degrees of freedom*, there will be  $f$  microscopic or macroscopic parameters that completely describe the microstates or macrostates of the system. (The microscopic parameters may be quantum numbers.) Macroscopic parameters define what kinds of microstates are possible, including their energies.

• **Thermodynamic Parameter** - (Sometimes simply called *state parameters*?)

(parameter values versus their mean values, mean values only well-defined in equilibrium...)

(What exactly do I mean by well-defined, and what does any other author have to say about it?)

A state parameter can be a *state function* (see below).

• **Internal, External Parameter** - Distill this information:

Reif says (pg 66): External parameters are macroscopically measurable independent parameters  $X_1, X_2, \dots, X_n$  that are known to affect the equations of motion (i.e., to appear in the Hamiltonian) of the system in question. Examples of such parameters are the applied magnetic or electric fields in which the system is located, or the volume  $V$  of the system (e.g, the volume  $V$  of the container confining the gas). The energy levels of the system depend then, of course, on the values of the external parameters. If a particular quantum state  $r$  of the system is characterized by an energy  $E_r$ , one can thus write the functional relation  $E_r = E_r(X_1, X_2, \dots, X_n)$ .

The macrostate of the system is defined by specifying the external parameters of the system and any other conditions to which the system is subject. For example, if one deals with an isolated system, the macrostate of the system might be specified by stating the values of the external parameters of the system (e.g., the value of the volume of the system) and the value of its constant total energy. The representative ensemble for the system is prepared in accordance with the specification of this macrostate; e.g., all systems in the ensemble are characterized by the given values of the external parameters and of the total energy. Of course, corresponding to this given macrostate, the system can be in any one of a very large number of possible microstates (i.e., quantum states).

...In a macroscopic description it is useful to distinguish between two types of possible interactions between such systems. In one case all the external parameters remain fixed so that the possible energy levels of the system do not change; in the other case the external parameters are changed and some of the energy levels are thereby shifted. We shall discuss these types of interaction in greater detail.

The first kind of interaction is that where the external parameters of the system remain unchanged. This represents the case of purely “thermal interaction”. As a result of the purely thermal interaction, energy is transferred from one system to the other. In a statistical description where one focuses

attention on an ensemble of similar systems ( $A + A'$ ) in interaction, the energy of every  $A$  system (or every  $A'$  system) does not change by precisely the same amount. One can, however, describe the situation conveniently in terms of the change in *mean* energy of each of the systems. The mean energy transferred from one system to the other as a result of purely thermal interaction is called “heat”. More precisely, the change  $\Delta\bar{E}$  of the mean energy of the system  $A$  is called the “heat absorbed” by this system; i.e.,  $Q \equiv \Delta\bar{E}$ .

Since the external parameters do not change in a purely thermal interaction, the energy levels of neither system are in any way affected. The change of mean energy of a system comes about because the interaction results in a change in the relative number of systems in the ensemble which are distributed over the fixed energy levels.

A system which cannot interact thermally with any other system is said to be “thermally isolated”, (or “thermally insulated”). It is easy to prevent thermal interaction between any two systems by keeping them spatially sufficiently separated, or by surrounding them with “thermally insulating” (sometimes called “adiabatic”) envelopes. These names are applied to an envelope provided that it has the following defining property: if it separates *any* two systems  $A$  and  $A'$  whose external parameters are fixed and each of which is initially in internal equilibrium, then these systems will remain in their respective equilibrium macrostates indefinitely. This definition implies physically that the envelope is such that no energy transfer is possible through it.

When two systems are thermally insulated, they are still capable of interacting with each other through changes in their respective external parameters. This represents the second kind of simple macroscopic interaction, the case of purely “mechanical interaction”. The systems are then said to exchange energy by doing “macroscopic work” on each other.

(“...appears in the Hamiltonian of the system...” seems a bit vague to me. At least, I’m not sure I’ve ever written a Hamiltonian for a thermodynamic system; I’ve only written Hamiltonians for the individual particulate constituents of such systems. )

“A non-thermal variable which can be freely controlled, and whose change involves the performance of work on the system, is called an external parameter.”

-From <http://www.jgsee.kmutt.ac.th/exell/Thermo/Systems.html>

(See site also for “non-thermal macroscopic variables”, “isometric set”, “mechanical equilibrium”, “isobaric set”, and “mechanical properties”.)

(Perhaps internal parameters are the microscopic, “hidden” parameters that are only known once a good model and (molecular and kinetic) theory are created.)

When external parameters are held constant, only purely “**thermal interactions**” are possible. (Does temperature always change for such processes? Does “thermal” always imply temperature?) (From “Work” below: “Macroscopic work” means that there must be a change in external parameters.)

The density of states  $\omega(Y_i)$ ; the variables  $Y_i$  are not necessarily external (See Reif pg 88)

- **Intensive, Extensive Parameters** - (link to homogeneous functions of order one and the ways in which one uses this information... in a function, each term must be of the same type)

A quantity is called:

- extensive when its magnitude is additive for subsystems (volume, mass, etc.)
- intensive when the magnitude is independent of the extent of the system (temperature, pressure, etc.)

Some extensive physical quantities may be prefixed in order to further qualify their meaning:

- specific is added to refer to [the quantity divided by its mass (such as specific volume)] or [the density of a quantity, such as specific volume (volume mass-density, (local) volume per mass), specific mass (mass volume-density, (local) mass per volume), or black-body specific intensity (intensity per (small) frequency interval)]
- molar is added to refer to the quantity divided by the amount of substance (such as molar volume)

There are also physical quantities that can be classified as neither extensive nor intensive, for example angular momentum, area, force, length, and time.

- **Natural Parameters** - natural variables (independent variables to describe the extensive state) “Unnatural” parameters would thus be...

See Gibbs phase rule and natural variables below.

- **Complete Set of Parameters** - ...

The set can be all extensive parameters (as with  $E(S, V)$ ) or all intensive parameters (as with  $G(T, P)$ , if numbers of particles are not involved) or a mix (as with  $F(T, V)$  and  $H(S, P)$ )

Barring the concept of partition functions (using the fundamental thermodynamic postulate and ensembles), the complete set is made of external parameters only.

- **State Function** - (a “function of state”) (I think that if a state parameter is considered to be a dependent variable of other independent parameters that form a “complete set”, then it is called a state function.)

- **Fundamental relations**/equations (relate to “the fundamental thermodynamic relation” / “the fundamental relation of thermodynamics”) (If you know a fundamental relation, you know everything about a thermodynamic system: you can calculate anything)

- \* energetic fundamental relation:  $U = U(S, V, N_1, N_2, \dots, N_r) = U(S, X_1, X_2, \dots, X_c)$  This is in the energy representation, where the set  $\{S, V, N_1, N_2, \dots, N_r\}$  is a complete set of independent state parameters and called the energetic extensive parameters, and the conjugate generalized forces are called the energetic intensive parameters. The equations of state are of the form  $T = T(S, V, N_1, N_2, \dots, N_r)$ ,  $P = P(S, V, N_1, N_2, \dots, N_r)$ ,  $\mu_j = \mu_j(S, V, N_1, N_2, \dots, N_r)$

- \* entropic fundamental relation:  $S = S(U, V, N_1, N_2, \dots, N_r) = S(X_0, X_1, X_2, \dots, X_c)$  This is in the entropy representation, where the set of variables  $\{X_0, X_1, X_2, \dots, X_c\}$  is called the entropic extensive parameters See Callen (section 2-3) for more (entropic intensive parameters  $F_k$  etc.)

- **Equation of State** (there are as many equations of state as there are parameters in the complete set of parameters; if you know all the equations of state, you know the fundamental relation, and thus everything about the thermodynamic system; Callen page 37: “relationships, expressing intensive parameters in terms of the independent extensive parameters, are called *equations of state*”)

You need to know all  $c$  equations of state to figure out the fundamental relation.<sup>2</sup>

...relations connecting the generalized forces, the external parameters, and the absolute temperature  $T$ . Such relations are called “equations of state” and are important since they relate parameters that are readily measured by experiment.

(Reif pg 238): “all expressions for generalized forces (i.e., all equations of state)”

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<sup>2</sup>For example, see Callen pg 63.

( $U$  or  $E$ ?)  $E = E(X_i)$ ;

$$\begin{aligned} dE &= \frac{\partial E}{\partial X_0} dX_0 + \frac{\partial E}{\partial X_1} dX_1 + \frac{\partial E}{\partial X_2} dX_2 + \cdots + \frac{\partial E}{\partial X_m} dX_m \\ &= T dS - \sum_k P_k dX_k \\ &= \delta Q - \delta W \end{aligned}$$

$S = X_0$ , ( $k\beta \equiv \frac{\partial S}{\partial E}$ , flipping derivative  $\Rightarrow T = \frac{\partial E}{\partial S}$ ),  $P_k \equiv -\frac{\partial E}{\partial X_k}$   $S = S(Y_i)$

$$\begin{aligned} dS &= \frac{\partial S}{\partial Y_0} dY_0 + \frac{\partial S}{\partial Y_1} dY_1 + \frac{\partial S}{\partial Y_2} dY_2 + \cdots + \frac{\partial S}{\partial Y_m} dY_m \\ &= k\beta dE - \sum_k F_k dY_k \\ &= \frac{1}{T} dE + \frac{1}{T} \delta W \end{aligned}$$

$E = Y_0$ , ( $k\beta \equiv \frac{\partial S}{\partial E}$ ),  $F_k \equiv -\frac{\partial S}{\partial Y_k}$

Eqn of State (EoS) Examples	
1. classical ideal gas law	8. BWRS EoS
2. Van der Waals EoS	9. Elliott, Suresh, Donohue EoS
3. Dieterici EoS	10. stiffened EoS
4. virial EoS	11. ultrarelativistic EoS
5. Redlich-Kwong EoS	12. ideal Bose EoS
6. Soave EoS	13. Birch-Murnaghan EoS (1944)
7. Peng-Robinson EoS	

### – Independent, Dependent Parameters

- **Conjugate Parameters** - Often called conjugate variables. (Show how they work in general, fundamental differential relation of thermodynamics; generalized force and displacement pairs, called conjugate pairs;  $\delta S = T \delta S$ , and  $\delta W$  explained below)  
For auxiliary entropies (Massieu functions), conjugate pairs are called affinities (generalized force) and fluxes (generalized displacement). (right?)

- **Process**

Types:

- Adiabatic: involving neither loss nor acquisition of heat. (also, for bndys: impassable to heat) ( $a$ - “not”,  $-dia$ - “through”,  $-bat(os)$ - “passable”,  $-ic$ ) (aka isocaloric)
- Isothermal: temperature remains constant.
- Isobaric: pressure remains constant.
- Isochoric: volume remains constant.
- *Isosomething*: the *something* variable remains constant. (E.g., isoenergetic, isoentropic or isentropic, isoenthalpic, etc.)
- Quasi-static: “slow”, such that the system is always infinitesimally close to an equilibrium state “slow” means taking longer than the relaxation time for reaching equilibrium after a disturbance
- Reversible: (turns out to be isentropic)

- **Equilibria: Mechanical, Electromagnetic, Chemical, and Thermal** -  
 (macroscopic mechanical equilibrium versus microscopic “thermal equilibrium”)  
 (chemical equilibrium includes phase equilibrium, right?)  
 (chemical and thermal equilibria, and most mechanical equilibria, are really just specific forms of electromagnetic equilibrium in its general, dynamical sense; mechanical equilibrium also includes gravitational equilibrium)  
 (Well, thermal and chemical equilibria seem to be both microscopic and macroscopic phenomena)  
 (A chemical reaction may be endothermic, exothermic)  
 (Mechanical work on a gas may heat or cool it)  
 (What about endergonic and exergonic processes? ... could this be like a hot gas expanding and a cool gas contracting?)
- **Thermodynamic Equilibrium** - A system in thermodynamic equilibrium (with itself or with its surrounding environment) is a system in mechanical, electromagnetic, chemical, and thermal equilibrium. All macroscopic parameters describing a system in thermodynamic equilibrium are time-independent.  
 (Quasi-static processes, partial equilibria, metastable equilibrium (Callen page 15) etc.)  
 (Quasi-static processes may be reversible or irreversible)  
 (Irreversible processes may be quasi-static or non-quasi-static)  
 (Reversible processes must be quasi-static)

Local versus Global Thermodynamic Equilibrium: It is important to note that this local equilibrium applies only to massive particles. In a radiating gas, the photons being emitted and absorbed by the gas need not be in thermodynamic equilibrium with each other or with the massive particles of the gas in order for LTE to exist.

Furthermore, the parameters that describe equilibrium states are **not allowed to depend on past states**, so we are free of hysteresis and other “memory-retaining” effects. (See Callen, Section 1-5.)

Callen page 15: “Operationally, a system is in an equilibrium state if its properties are consistently described by thermodynamic theory!”

- **Fundamental Thermodynamic Postulate:** An isolated system in equilibrium is equally likely to be in any of its accessible states (i.e., microstates?).

### 5.3 Thermodynamic Quantities

- **$E$**  - the total energy of a system (with respect to some reference frame and reference state).  
 (Macroscopically, energy is the ability to do work and implies “the potential for causing changes”.)  
 $E = K + P$ ; the total energy is made up of kinetic energy  $K$  and potential energy<sup>3</sup>  $P$ , which can be broken down further into sub-terms (see below).  
 $E = E_{\text{ext}} + U$ ; the total energy is made up of the “external” energy  $E_{\text{ext}}$  of the system and the “internal” energy  $U$  of the system. (See elaboration in next two entries.)
- Sometimes it is convenient to distinguish macroscopic (“a”) and microscopic (“i”) scales (and maybe even intermediate scales), which are context-dependent. Thus, we get these energy terms:  

$$E = K_{\text{ext}}^{\text{a}} + K_{\text{ext}}^{\text{i}} + K_{\text{int}}^{\text{a}} + K_{\text{int}}^{\text{i}} + P_{\text{ext}}^{\text{a}} + P_{\text{ext}}^{\text{i}} + P_{\text{int}}^{\text{a}} + P_{\text{int}}^{\text{i}}$$
- $\Delta E = Q - W$ ; we can separate change of systemic energy into “heat absorbed by the system”  $Q$  and “work done by the system”  $W$ . (See entries below. ...Is  $Q = \Delta K_{\text{int}}^{\text{i}}$ ?)

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<sup>3</sup>In these notes, this symbol,  $P$ , stands for pressure everywhere except this entry and the next two. Note also that  $\mathcal{P}$  denotes a probability and  $\mathbf{P}$  denotes a polarization.

- $dE = \bar{d}Q - \bar{d}W$ ;
- A fairly general expression of change in energy is  
 $dE = TdS \mp gh M_i dn_i + V\sigma_{jk} d\varepsilon_{jk} \mp \phi_\ell dQ_\ell + V\mathbf{E}_e \cdot d\mathbf{D} + V\mathbf{H}_m \cdot d\mathbf{B} + \mu_m dN_m + \mu_n dN_{cn}$ ,  
 summing over repeated indices. (See below for explanation of terms.)

Electromagnetic energy (I think this is sometimes called “pure” energy by popularizers of physics, since it’s energy that is not associated with matter/mass, but I would discourage this.), (the energy associated with electromagnetic radiation is called radiant energy)

- $E_{\text{ext}}$  - the external energy of a system is the energy that would disappear if one moved to the rest frame of the system and caused all objects outside of the system to cease to exist.

$E_{\text{ext}} = K_{\text{ext}} + P_{\text{ext}}$ ; “external” kinetic  $K_{\text{ext}}$  and “external” potential  $P_{\text{ext}}$  energies of the system.  
 $E_{\text{ext}} = K_{\text{ext}}^a + K_{\text{ext}}^i + P_{\text{ext}}^a + P_{\text{ext}}^i$ ;  $a \Rightarrow$  macroscopic,  $i \Rightarrow$  micro.

- $U$  - the internal energy of a system (always in the rest frame of the system) is the energy that would remain if one moved to the rest frame of the system and caused all objects outside of the system to cease to exist.

$U = K_{\text{int}} + P_{\text{int}}$ ; “internal” kinetic  $K_{\text{int}}$  and “internal” potential  $P_{\text{int}}$  energies of the system.  
 $U = K_{\text{int}}^a + K_{\text{int}}^i + P_{\text{int}}^a + P_{\text{int}}^i$ ;  $a \Rightarrow$  macroscopic,  $i \Rightarrow$  micro.

$K_{\text{int}}^i$ , the microscopic internal kinetic energy, may also be called the “heat energy” (Some may say this is not proper use of the word “heat”, but it seems to be used commonly even in physics courses. In this term, the word “heat” does not imply microscopic work as it does in other contexts.)

$U(S, V, N_1, N_2, \dots)$  or  $U(\text{other complete set of variables})$

(Internal energies: both macroscopic energies from visible “ordered” states or macroscopic components and microscopic energies from random, disordered motions and configurations of the particles)

(Microscopic energies: translational kinetic energy, vibrational and rotational kinetic energy, and potential energy from intermolecular forces)

(Thermal energy: microscopic kinetic energies? and potential energies?)

(?: Wikipedia - “Thermal energy is the internal energy of a thermodynamic system at equilibrium. The flow of thermal energy from one system to another is called heat. Thermal energy is a measure of the total vibrational energy in all the molecules and atoms in a certain substance. Thermal energy is composed of both kinetic and potential energy. The kinetic energy is from the random motion of the particles, and the potential energy originates from the repulsive electromagnetic force between the electrons of atoms that are close to each other.”)

Can derive:  $U = TS - PV + \mu N$  ( $TS$ : “(stored) thermal energy”;  $-PV$  “(stored) compressive energy”)

- $W$  - the macroscopic mechanical work done by the system of interest.  
 (Should this be called “generalized work” or can it all really be derived from Newtonian work, with a force acting over a distance?)

(We are usually outside of the system, looking at it and saying, “What (work) are you doing for me?”)

“Macroscopic work” means that there must be a change in external parameters.

Each work term is a product of a generalized force  $P_k$  and its conjugate generalized displacement  $dX$ :  $dW = \sum_k P_k dX_k$

(Is it appropriate to consider  $P_k$  a generalized force “on the environment due to the system” and  $dX_k$  the conjugate displacement “of the (external) environment”?)

## Mechanical Work

- $(\pm?)V \sum_{ij} \sigma_{ij} d\varepsilon_{ij}$ : **stress-strain work**(?); work done by viscous fluids, or plastic and/or elastic solids, where  $\sigma$  is the stress tensor and  $\varepsilon$  is the strain tensor. (I think  $\sigma$  is the generalized force and  $Vd\varepsilon$  is the conjugate displacement.) This extends also to  $-\Gamma dl$ , the **elastic work** to change the length of a wire with tension  $\Gamma$  by  $dl$ , and  $-\gamma dA$ , the **surface work** to change the area of a membrane of surface tension  $\gamma$  by  $dA$ .

\*  $P dV$ : **pressure-volume work** or “PV work”; work done by a non-viscous fluid at pressure  $P$  through a change in volume  $dV$ , where  $P$  is the generalized force and  $V$  is the generalized displacement

(Note that that pressure acts to expand, while tension acts to contract... if explained correctly, this should make the signs obvious.)

Include partial pressure here

- $(\pm?)\psi dm$ : **gravitational work**; the work done in opposition to gravity (not in changing height but changing mass?).  $\psi dm = (gh) d(\sum_i M_i n_i) = \sum_i gh M_i dn_i$  (from Alberty [5])

### Chemical Work

- $\mu dN$ : (heat?)

If  $\mu dN$  were heat, then it would be included in  $dQ = T dS$ , but that does not seem to be the case.

$\mu$  - Chemical potential or Electrochemical potential: the generalized force for the generalized displacement of number of molecules (given that  $N_i$  refers to the number of “ $x$ ” molecules, the units of  $\mu_i$  are Joules per “ $x$ ” molecule.)

Sometimes the “chemical potential” is defined to be the electrochemical potential  $\mu$  minus the molar electrostatic energy.

\*  $\sum_i \mu_i dN_i$ : chemical work (without reactions), where  $N_i$  is the number of particles of the  $i$ th species

\*  $\sum_i \mu_i dN_{ci}$ : chemical work (with reactions), where  $N_{ci}$  is the number of particles of the  $i$ th component in the reaction(s)

### Electromagnetic Work

- $(\pm?)\sum_i \Phi_i dQ_i$ : work done by gaining a particle of the  $i$ th species (with charge  $Q_i$  in an electric potential  $\Phi_i$ ) (charge transfer)

- $-\mathbf{E}_e \cdot d\mathbf{p}$ : work done by a change in electric dipole moment  $\mathbf{p}$  in an electric field  $\mathbf{E}_e$

$$-V\mathbf{E}_e \cdot d\mathbf{D} = -V(\varepsilon_0\mathbf{E}_e \cdot d\mathbf{E}_e + \mathbf{E}_e \cdot d\mathbf{P}) = -Vd\left(\frac{\varepsilon_0}{2} |\mathbf{E}_e|^2\right) - (\mathbf{E}_e \cdot d\mathbf{p})$$

$$= dW_e + dW_{\text{polarization}}$$

- $-\mu_0\mathbf{H}_m \cdot d\mathbf{m}$ : work done by a change in magnetic dipole moment  $\mathbf{m}$  in a magnetic field  $\mu_0\mathbf{H}$

$$-V\mathbf{H}_m \cdot d\mathbf{B} = -V(\mu_0\mathbf{H}_m \cdot d\mathbf{H} + \mu_0\mathbf{H}_m \cdot d\mathbf{M}) = -Vd\left(\frac{\mu_0}{2} |\mathbf{H}_m|^2\right) - (\mu_0\mathbf{H}_m \cdot d\mathbf{m})$$

$$= dW_m + dW_{\text{magnetization}}$$

(What about  $VdP$ ,  $Nd\mu$ , etc?, Gibbs-Duhem relation)

We will also add  $TdS$  to this formalism, but it is the heat term rather than a work term.

In (fair) generality, summing over repeated indices,

$$dW = \pm gh M_i dn_i - V\sigma_{jk} d\varepsilon_{jk} \pm \phi_\ell dQ_\ell - V\mathbf{E}_e \cdot d\mathbf{D} - V\mathbf{H}_m \cdot d\mathbf{B} - \mu_m dN_m - \mu_n dN_{cn}$$

- $\Delta_x \bar{E}$  - the change in mean energy calculable from the change of external parameters (i.e., due to macroscopic work done on a system)

- $Q$  - the “heat absorbed by a system”;  $-Q$  is the “heat given off” by the system

$$Q \equiv \Delta \bar{E} + W \text{ or } Q = \Delta \bar{E} + W$$

Heat as energy exchange, definitions:

- Heat is defined as the transfer of energy to a body that does not involve work—or those transfers of energy that occur only because of a difference in temperature. (from [http://pruffle.mit.edu/3.00/Lecture\\_06\\_web/node2.html](http://pruffle.mit.edu/3.00/Lecture_06_web/node2.html))
- Here,  $Q$  is simply defined to be the change in mean energy of the system *not* due to a change in the external parameters. It measures the change in energy due to “purely thermal” interactions. (However, this view, which is taken from Reif (pg 73 etc), implies that  $\mu dN$  is a heat term in addition to  $TdS$ , or does it? If we weigh the sample, then  $N$  could possibly be an external parameter, no? Or would we have to know what particles are involved and their masses to do that... and what about combinations of different particles with different masses?)
- “An energy transfer via the hidden atomic modes is called *heat*.” (Callen pg 8)

The word “heat” may refer to

- *v.* to increase the temperature of
- *n.* “thermal energy” or “heat energy”
- *n.* the average kinetic energy of a body (which is a state variable, and a body *has* heat in this usage)
- *n.* “heat... is the random motion of molecules” (from The Mechanical Universe: the gyroscope episode)
- *n.* electromagnetic radiation (esp. infrared (since humans and other everyday objects absorb it so well?) (other frequencies?)) (as in “I feel the heat from the lamp”)
- *n.* an environment that has the capacity to heat a body (as in “stepping out into the heat”  $\approx$  “stepping out into the hot air”)

Talk about “latent heat” and methods of “heat transfer/flow” (redundant?) (heat as average kinetic energy versus heat as abstract energy transfer)

“heat reservoir” or “thermal reservoir” or “heat bath” (perhaps goes with the statistical material below, since they have enormous “degrees of freedom”)

**Thermal radiation** (electromagnetic radiation emitted from the surface of an object which is due to the object’s temperature)

- **S** - Entropy... different definitions

$S \equiv k \ln \Omega(E)$  or  $S \equiv k \ln \left( \frac{\omega(E)}{[\omega(E)]} \right)$  or  $S \equiv k \ln \omega(E)$  (if only differences matter, then perhaps we should only define differences...)

$$S(E \pm \delta E) \equiv k \ln \Omega(E, \delta E) = k \ln(\omega(E)2\delta E) = k \ln \left( \frac{\omega(E)}{[\omega(E)]} \right) + k \ln \left( \frac{2\delta E}{[\delta E]} \right) \approx k \ln \left( \frac{\omega(E)}{[\omega(E)]} \right)$$

“information function” is the same as the reduced entropic function in thermodynamics. (What about the measurability of  $S$ ?)

Callen Postulates:

1. There exist particular states (called equilibrium states) of simple systems that, macroscopically, are characterized completely by the internal energy  $U$ , the volume  $V$ , and the mole numbers  $N_1, N_2, \dots, N_r$  of the chemical components.
2. There exists a function (called the entropy  $S$ ) of the extensive parameters of any composite system, defined for all equilibrium states and having the following property: The values assumed by the extensive parameters in the absence of an internal constraint are those that maximize the entropy over the manifold of constrained equilibrium states.
3. The entropy of a composite system is additive over the constituent subsystems. The entropy is continuous and differentiable and is a monotonically increasing function of the energy.

- The entropy of any system vanishes in the state for which  $(\partial U/\partial S)_{V,N_1,N_2,\dots,N_r} = 0$  (that is, at the zero of temperature).

Entropy may be introduced using the Clausius theorem (1854):  $\oint \delta Q/T \leq 0$  in a cyclic process (equality holding for reversible processes).

### Measuring Entropy

“Let’s say you pour some cold water into some hot water. What happens to the entropy? Why?”

- **$T, \beta$**  - Absolute temperature  $T$ , Temperature parameter<sup>4</sup>  $\beta$   
 Thermodynamic definition?: “Temperature is, by definition, proportional to the average internal energy of an equilibrated neighborhood.” (From Wikipedia Thermodynamic Equilibrium entry)  
 From Goldstein [4]: “. . . by the equipartition theorem of kinetic theory, the average kinetic energy of each atom is given by  $\frac{3}{2}kT$ , . . . a relation that in effect is the definition of temperature.”  
 Statistical definition:  $\beta \equiv \frac{\partial \ln \omega}{\partial E}, T \equiv \frac{1}{k\beta}$   
 More detail:  $\beta = \left. \frac{\partial \ln \omega'}{\partial E'} \right|_{E'=E_{\text{tot}}}$  where  $\omega'$  is for the heat reservoir of energy  $E'$  that the system of interest is in contact with, and the total energy of the two systems is  $E_{\text{tot}}$
- **Thermodynamic Potentials** - (aka auxiliary energy functions, thermodynamic free energies, free energy functionals); the total amount of energy in a physical system which can be converted to do work. Legendre transforms of  $U$ .
  - **$F \equiv U[T]$**  - Helmholtz free energy (sometimes  $A$ ); the amount of thermodynamic energy which can be converted into work at constant temperature and volume. In chemistry, this quantity is called work content. (or is it just the “measures the ‘useful’ work obtainable”? Wikipedia lookup)  

$$F \equiv U - TS \qquad dF(T, V) = -SdT - PdV$$
  - **$H \equiv U[P]$**  - Enthalpy or heat content/function; for a simple system, with a constant number of particles, the difference in enthalpy is the maximum amount of thermal energy derivable from a thermodynamic process in which the pressure is held constant. Also, colloquially, enthalpy is the total amount of energy one needs to provide to create the system and then place it in the atmosphere:  

$$H \equiv U + PV \qquad dH(S, P) = TdS + VdP$$
  - **$G \equiv U[T, P]$**  - Gibbs free energy; the amount of thermodynamic energy in a fluid system which can be converted into work at constant temperature and pressure. This is the most relevant state function for chemical reactions in open containers. (Wikipedia lookup)  

$$G \equiv U - TS + PV \qquad dG(T, P) = -SdT + VdP$$
  - **$U[T, \mu]$**  - Grand Canonical Potential...
- **Massieu Functions** - Legendre transforms of  $S$ .

## 5.4 Statistical Mechanics Terms

- **$\Phi(E)$**  - the number of states with energy less than  $E$ .  
 There must, of course, be a ground state if this quantity is to be finite.  
 $(\Phi(E; X_i), \Phi(X_i; X_j))$

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<sup>4</sup>“thermodynamic beta” as opposed to the “relativistic beta”

- $\Omega(E)$  - the number of states with energy in the interval  $[E, E + \delta E)$  (or  $(E, E + \delta E)$ ?). (Actually, a function of  $E$  and the external parameters of the system.)

This definition of  $\Omega(E)$  depends on the selection of the interval  $\delta E$ . The magnitude of  $\delta E$  determines the precision within which one chooses to measure the energy of the system. (How does that relate to  $\delta E$ ?) We assume that  $\Omega(E)$  is an approximately smooth function, that  $\Omega(E) \rightarrow 0$  as  $\delta E \rightarrow 0$ , and that  $\Omega(E)$  is expressible as a Taylor series in powers of  $\delta E$ ; while  $\delta E$  is large compared to the spacing between the possible energy levels of the system, it is macroscopically small enough for the relation  $\Omega(E) = \omega(E)\delta E$  to be approximately true, where the higher order Taylor terms are negligible and  $\omega(E)$  is a smooth function.

- $\Omega(E; \mathbf{y}_k)$  - the number of states with energy in the interval  $[E, E + \delta E)$  (or  $(E, E + \delta E)$ ?), and parameter  $y$  with the value  $y_k$  (or quantum state  $y_k$ )?.

- $\rho$  - Density of States (the number of states per some quantity)

The density may be an energy-density, momentum-density, wavevector-density, etc.:

$\rho(E), \rho(\epsilon), \rho(\mathbf{p}), \rho(\mathbf{k}), \rho(\mathbf{n}),$  etc.

$\omega(E)$  - the density of states ( $\Omega(E)/\delta E$  as  $\delta E \rightarrow 0$ ).

$\omega(Y_i)$ ; the variables  $Y_i$  are not necessarily external (See Reif pg 88)

Variously written as  $\omega(E), n(E), \rho(E)$  (or  $\omega(\epsilon), n(\epsilon), \rho(\epsilon)$ )

Note that “density of states” may refer to a function of parameters other than energy:

( $\omega$  is preferable to  $\Omega$  with respect to precision of mathematical argument.  $\Omega$  seems to be the traditional choice and simplifies unit issues.)

Unless there is some bound on the energy of the states,  $\int_{-\infty}^{\infty} \omega(E) dE$  is undefined

$$\int_{-\infty}^{\infty} \omega(E) e^{-\beta E} dE = 1$$

- $f$  - Occupancy

$f(\epsilon) d\epsilon$ : This is the average number (or number volume-density) of particles that occupy quantum states with energy between  $\epsilon$  and  $\epsilon + d\epsilon$ , right?

- $n_r$  - the number of particles (in an ensemble element system) that are in a particle quantum state labeled by  $r$

$$\bar{n}_r = -\frac{1}{\beta} \frac{\partial \ln Z}{\partial \epsilon_r}$$

- $w$  - Probability Energy-Density (probability per increment of energy)

- $\rho(\mathbf{q}, \mathbf{p})$  - the “distribution function” (i.e., the probability density function of states in phase space, a.k.a. statistical distribution function)

$$dw = \rho(q_i, p_i) dq dp$$

- $d\mathbf{w}$  - the infinitesimal probability that a (sub)system occupies a state within the infinitesimal (i.e., macroscopically tiny) region between  $q_i, p_i,$  and  $q_i + dq_i, p_i + dp_i,$  with volume  $V = dq dp.$

- $w$  - the probability that a (sub)system, when observed at an arbitrary instant, will be found in a state within the region in phase space between  $q_i, p_i,$  and  $q_i + \Delta q_i, p_i + \Delta p_i,$  with volume  $V = \Delta q \Delta p.$  (perhaps call it  $w_V$ )

$$(w(E) = \int dw(E) = \int \rho(q_i, p_i) dq dp)?$$

$w = \lim_{T \rightarrow \infty} \frac{\Delta t}{T}$ , where  $\Delta t$  is the time spent in the specified region in phase space and  $T$  is... the total time that the (sub)system spends in any region of phase space?

I don't see how it can really refer to a subsystem because then it would not have anything to do with some of the  $q_i$  and  $p_i$ ; it would be independent of some of them (so maybe it would have a Dirac delta associated with those?)

- $\int_{-\infty}^{\infty} w(E) dE = \int_{E_{\min}}^{\infty} w(E) dE = 1 = \int_{-\infty}^{\infty} \omega(E) e^{-\beta E} dE$

- $\mathcal{P}$  - probability  
The caligraphic  $\mathcal{P}$  is used to avoid confusion with pressure  $P$ , polarization  $\mathbf{P}$ , and potential energy  $\mathcal{P}$ .
- **Statistical Ensemble** - Mostly, we're interested in (or can only measure) mean quantities (mean with respect to (local?) space and time). We use a statistical approach and model the actual system using an ensemble of systems, one system for each of the physically possible distinguishable configurations of the actual system that obey the given constraints. (According to the postulate... equiprobability...) (stationary ensemble) (mathematicians prefer "probability space")
  - **Microcanonical ensemble** ( $\Omega$ ) - an ensemble of systems, each of which is required to have the same total energy (i.e. thermally isolated?) (Each system is isolated and in equilibrium).  $\Omega(U, V, N) = e^{\beta TS}$  (?)
  - **Canonical ensemble** (Isothermal-Isochoric) - an ensemble of systems, each of which can share its energy with a large heat reservoir or heat bath. The system is allowed to exchange energy with the reservoir, and the heat capacity of the reservoir is assumed to be so large as to maintain a fixed temperature for the coupled system.  $Z(T, V, N) = e^{-\beta A}$ ,  $\zeta$  (?)  
 $Z = \sum_i e^{-\beta E_i} = e^{-\beta F}$
  - **Grand Canonical ensemble** - an ensemble of systems, each of which is again in thermal contact with a reservoir. But now in addition to energy, there is also exchange of particles. The temperature is still assumed to be fixed.  $\Xi(T, V, \mu) = e^{\beta PV}$  (?)
  - **Isothermal-Isobaric ensemble** - an "ensemble where the system is allowed to exchange energy with a heat bath of temperature  $T$  and the volume can also change though its mean value is tuned by the pressure  $P$  applied. It is also called the  $(T, P, N)$ -ensemble, as the third quantity kept constant is the number of particles  $N$ . This ensemble plays an important role in chemistry as chemical reactions are usually carried out under constant pressure condition. The partition function is given as  $\Delta(N, T, P) = \int \sum_i \exp -\beta(E_i + PV)dV$ . The characteristic state function of this ensemble is the Gibbs free energy since  $\Delta = e^{-\beta G}$ ."
  - **Isoenthalpic-Isobaric ensemble** -  $(S, P, ?)$
- **Partition Functions** - ("Boltzmann sum over states" or "sum over levels with degeneracy/multiplicity") (functions that are sums, the partition function "encodes the underlying physical structure of the system" (?) or "encodes the statistical properties of a system in thermodynamic equilibrium" (??)) (LOOK UP partition function, canonical ensemble, and Fermi energy on WIKIPEDIA)
  - Types
    - \* (Microcanonical partition function?)
    - \*  $Z$  - (Canonical) partition function  
 $Z \equiv \sum_r e^{-\beta E_r}$ ,  $Z = \frac{\zeta^N}{N!}$   
in the classical approx.  $Z = \int \dots \int e^{-\beta E(q_1, \dots, p_f)} \frac{dq_1 \dots dp_f}{h_0^f}$
    - \*  $\zeta$  - (individual particle, or subsystem?) (canonical?) partition function  
 $\zeta \equiv \sum_r e^{-\beta \epsilon_r}$  (?)  
 $\zeta = \frac{V}{h_0^3} \int_{-\infty}^{\infty} e^{-\beta \mathbf{p}^2/2m} d^3p$  (7.2.5) for noninteracting gas in
    - \*  $\mathcal{Z}$  - a Grand (Canonical) partition function  
 $\mathcal{Z} \equiv \sum_N Z(N) e^{-\alpha N}$  (From Reif pg 347)
    - \*  $\Xi$  - Grand Canonical partition function(al?) (From ThermoPotentials paper)  
(What are the arguments of the partition function? If it ever takes a function as an argument then it may be considered properly as a functional if it returns a constant (but I don't think

it does). Whether a quantity is considered an element of the complete set of parameters determines whether it is a mere parameter or a function...)

- \*  $\Delta$  - Isothermal-Isobaric partition function
- \*  $Q$  - Canonical Ensemble partition function
- \* Integral Forms and the “Density of States”!!! (Planck’s constant, multidimensional forms, and “geometric factor”)

– Properties

- \* Energy is arbitrary up to additive constant  $\epsilon_0$ , so  $Z' = \sum_r e^{-\beta(E_r + \epsilon_0)} = e^{-\beta\epsilon_0} Z$   
 $\ln Z' = \ln Z - \beta\epsilon_0$  and  $\bar{E}' = -\frac{\partial \ln Z'}{\partial \beta} = -\frac{\partial \ln Z}{\partial \beta} + \epsilon_0 = \bar{E} + \epsilon_0$   
 but entropy and all expressions for generalized forces (all eqns of state) are unchanged.
- \*  $Z_3 = Z_1 Z_2$  for a system (of degrees of freedom) made of two weakly interacting subsystems (of dof) with partition functions  $Z_1$  and  $Z_2$ . (E.g., in a diatomic gas  $Z_1$  could refer to dof of translational motion of centers of mass, and  $Z_2$  could refer to dof of rotation of molecules about their centers of mass.)

- **Boltzmann Factor** -  $e^{-\beta E}$ , aka “canonical weighting factor”<sup>5</sup>

$$Z \equiv \sum_r e^{-\beta E_r} = e^{-\beta F} \quad (!)$$

$$\Delta = e^{-\beta G} \quad (!)$$

$$P_r = C e^{-\beta E_r} = \frac{1}{Z} e^{-\beta E_r}$$

Valid for an ensemble of systems in contact w/ a reservoir

Associated with Canonical Ensembles or Distributions

(How universal is it?)

- $\bar{y}$  - the mean value of the parameter  $y$  at equilibrium

$$\bar{y} = \sum_k y_k \mathcal{P}(y_k) = \frac{\sum_k y_k \Omega(E; y_k)}{\Omega(E)}$$

$$\bar{y} = \sum_r y_r P_r = C \sum_r y_r e^{-\beta E_r} = \frac{1}{Z} \sum_r y_r e^{-\beta E_r}$$

$$\bar{y} =$$

- **Statistical Frameworks / Models for Ideal Gases** -

– **MB** Maxwell-Boltzmann Statistics

$$\bar{n}_r = \frac{N}{Z} e^{-\beta \epsilon_r};$$

the “Maxwell-Boltzmann distribution”

– **FD** Fermi-Dirac Statistics

$$\bar{n}_r = \frac{1}{e^{\alpha + \beta \epsilon_r} + 1};$$

the “Fermi-Dirac distribution”

$$\bar{n}_r = \frac{1}{e^{\beta(\epsilon_r - \mu)} + 1}, \text{ where } \mu \equiv -\frac{\alpha}{\beta} = -kT\alpha \text{ is called the “Fermi energy” of the system}$$

( $\mu$  is also the chemical potential)

– **BE** Bose-Einstein Statistics

$$\bar{n}_r = \frac{1}{e^{\alpha + \beta \epsilon_r} - 1};$$

the “Bose-Einstein distribution”

Photon statistics:  $\bar{n}_r = \frac{1}{e^{\beta \epsilon_r} - 1}$ ; the “Planck distribution”

– Other statistics: anyon, braid, etc.

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<sup>5</sup>See Callen, pg 434

- **“Fermi” Terms:** Fermi level, energy, sea, function, velocity, more?  
 “Fermi level” is the term used to describe the top of the collection of electron energy levels at absolute zero temperature. This concept comes from Fermi-Dirac statistics. Electrons are fermions and by the Pauli exclusion principle cannot exist in identical energy states. So at absolute zero they pack into the lowest available energy states and build up a “Fermi sea” of electron energy states. The Fermi level is the surface of that sea at absolute zero where no electrons will have enough energy to rise above the surface. (Relate to valence band, band gap, conduction band.)

## 5.5 Quantities Defined for Proofs

- $\Phi_i(\epsilon)$  - the number of possible values which can be assumed by the quantum number associated with the  $i^{th}$  degree of freedom when it contributes to the system an amount of energy  $\epsilon$  or less.  
 Used in deriving the crude approximation  $\Omega(E) \approx E^f$  ( $\Omega(U) \approx U^f$ ?)
- $Z_s(N)$  - ...  
 $Z_s = Z_s(N) = Z_s(N, n) = Z_s(N, n, \beta)$   
 Used in defining  $\alpha_s$  and then (defining/deriving)  $\alpha$

## 5.6 Comments on Terms

- Functions: There are various quantities and functions that are given names that include the word “function”, while other functions are not explicitly named as “functions”.
  - “Natural function” - Callen says (pg 183) that  $U$  is a natural function of  $V$  and  $S$  (i.e., its natural independent variables are  $V$  and  $S$ ),  $F$  is a natural function of  $V$  and  $T$ , and so on...
  - “State function”
  - “Partition function”
- “Relation” versus “Equation”: In thermodynamics the word relation seems to be preferred over the word equation for some reason. At the very least, this helps to distinguish between the electromagnetic *Maxwell equations* and the thermodynamic *Maxwell relations*.

## 5.7 More Thermodynamic Quantities

- $\eta$  - Efficiency
- $C_Y$  - Heat capacity at constant ( $Y$  quantity name)

$$C_Y \equiv \left( \frac{dQ}{dT} \right)_Y$$

Specific heat

“Specific heat per mole”, “Specific heat per gram”

- $\mu$  Joule-Thomson Coefficient
- $\gamma$  Specific Heat Ratio
- $\kappa$  Isothermal Compressibility (or Isothermal Coefficient of Compressibility):

$$\kappa \equiv -\frac{1}{V} \left( \frac{\partial V}{\partial p} \right)_T$$

- Bulk Modulus: the reciprocal of the isothermal compressibility

- Isobaric Coefficient of Thermal Expansion

$$\frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_p$$

- $\alpha$  Volume Coefficient of Expansion

$$\alpha \equiv \frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_p$$

- Isochoric Coefficient of Tension

$$\frac{1}{p} \left( \frac{\partial p}{\partial T} \right)_V$$

- Fugacity (define this)

$$y = e^{-u}$$

## 6 Laws and Relations

CHECK HERE: [http://en.wikipedia.org/wiki/Table\\_of\\_thermodynamic\\_equations](http://en.wikipedia.org/wiki/Table_of_thermodynamic_equations)

### Some Equations

$$\omega = \omega(E, \dots) \quad Z = Z(\beta, \dots) \stackrel{c}{=} Z(T, V, N)?$$

$$\ln Z = \ln \omega - \beta E + \ln \Delta^* E^0$$

In Terms of $\omega$	In Terms of $Z$
$E = -\frac{\partial \ln \omega}{\partial \beta}$	$E = -\frac{\partial \ln Z}{\partial \beta} \quad (?)$
$S \equiv k \ln \omega$	$(\Delta E)^2 = \frac{\partial^2 \ln Z}{\partial \beta^2} = -\frac{\partial E}{\partial \beta}$ $S = k(\ln Z + \beta E) = k(\ln Z - \beta \frac{\partial \ln Z}{\partial \beta})$
$F = \dots$	$F = -kT \ln Z$
$\beta \equiv \frac{\partial \ln \omega}{\partial E}$	$\beta = \dots$
$P_k = \dots$	$P_k = \frac{1}{\beta} \frac{\partial \ln Z}{\partial X_k} = kT \frac{\partial \ln Z}{\partial X_k}$
$P = \dots$	$P = kT \frac{\partial \ln Z}{\partial V} \neq \left( \frac{\partial E}{\partial V} \right)_S \quad (?)$
$c_v = \dots$	$c_v = k\beta^2 \frac{\partial^2 \ln Z}{\partial \beta^2} \quad (?)$
$\mu_j = \dots$	$\mu_j = -kT \frac{\partial \ln Z}{\partial N_j}$
$\alpha = \dots$	$\alpha = \frac{\partial \ln Z}{\partial N}$
$\alpha = -\beta \mu$ (no $\mu_j$ ?)	
$\bar{n}_s = \dots$	$\bar{n}_s = -\frac{1}{\beta} \frac{\partial \ln Z}{\partial \epsilon_s}$ $(\Delta n_s)^2 = -\frac{1}{\beta} \frac{\partial \bar{n}_s}{\partial \epsilon_s} = \frac{1}{\beta^2} \frac{\partial^2 \ln Z}{\partial \epsilon_s^2}$

$$\beta = \frac{\partial \ln \omega}{\partial E} \Leftrightarrow \frac{1}{T} = \frac{\partial S}{\partial E}$$

$$P_k = \frac{1}{\beta} \frac{\partial \ln \omega}{\partial X_k} \Leftrightarrow \frac{P_k}{T} = \left( \frac{\partial S}{\partial X_k} \right)$$

## Laws of Thermodynamics

### Deriving the Laws

- The Liouville equation is integral to the proof of the fluctuation theorem from which the second law of thermodynamics can be derived.

### Terse Statements

0. Zeroth Law: Thermal equilibrium is a transitive property.
1. First Law:  $\Delta U = Q - W$  (Heat defined or Dichotomy declared.) (Why not  $\Delta E$ ?)
2. Second Law: a)  $\Delta S \geq 0$  for adiabatic processes linking macrostate equilibria.  
b)  $dS = \frac{dQ}{T}$  for quasi-static infinitesimal processes.
3. Third Law:  $S \rightarrow S_0$  as  $T \rightarrow 0^+$  for any system.

### Full Statements

#### 0. Zeroth Law

Two systems that are in thermal equilibrium with a third system are in thermal equilibrium with each other.

#### 1. First Law

An equilibrium macrostate of a system can be characterized by a quantity  $U$  (called “internal energy”) which has the property that, for an isolated system,

$$U = \text{constant.}$$

When the system is allowed to interact with its environment (i.e., when the system is not isolated), the resulting change in  $U$  can be written in the form

$$\Delta U = Q - W,$$

where  $W$  is the macroscopic work done *by* the system as a result of the system’s change in external parameters. The quantity  $Q$  is the “heat absorbed by the system”.

(If  $Q$  is defined by this equation, then this is the definition of  $Q$ . If  $Q$  is defined in terms of physical processes, and conservation of energy is assumed, then this is a postulate stating that there are only two forms of energy exchange: work and heat.)

#### 2. Second Law(s)

An equilibrium macrostate of a system can be characterized by a quantity  $S$  (called “entropy”), which has the properties that

- (a)  $\Delta S \geq 0$  for a thermally isolated system (i.e., for adiabatic processes) where the system goes from one macrostate to another,
- (b)  $dS = \frac{dQ}{T}$  for a quasi-static infinitesimal process (heat reservoirs, etc.), given that the system is not isolated and absorbs heat  $dQ$ , and where  $T$  (called “absolute temperature”) is a quantity characteristic of the macrostate of the system.

#### 3. Third Law

$S \rightarrow S_0$  as  $T \rightarrow 0^+$  for any system, where  $S_0$  is a constant independent of all parameters of the system.

## Restatements of Thermodynamic Laws

- Allen Ginsberg:
  1. First: You can't win.
  2. Second: You can't break even.
  3. Third: You can't quit.
- Wikipedia:
  0. Zeroth: If two thermodynamic systems are in thermal equilibrium with a third, they are also in thermal equilibrium with each other.
  1. First: In any process, the total energy of the universe remains constant.
  2. Second: There is no process that, operating in a cycle, produces no other effect than the subtraction of a positive amount of heat from a reservoir and the production of an equal amount of work.
  3. Third: As temperature approaches absolute zero, the entropy of a system approaches a constant.
- C. Combined Law:  $dE - TdS + PdV \leq 0$ . (First + Second)
- First Law
  - (1865) “The energy of the universe is constant.” –Claussius
  - A state function, called the internal energy, exists for any physical system—and the change in the internal energy during any process is the sum of the work done on the system and the heat transferred to the system.
  - The work done on a system during an adiabatic process is a state function and numerically equal to the change in internal energy of the system.
  - Interpretations:
    - \* A restriction on the processes that occur in any system.
    - \* A definition.
    - \* A bookkeeping device.
- (1865) Second (a): “The entropy of the universe tends to a maximum.” –Claussius
- (1874) Thomson formally states the second law of thermodynamics
- (1906) Nernst presents a formulation of the third law of thermodynamics. (The third law of thermodynamics may also be called the Nernst heat theorem.)
- (What about other heat laws, such as “the heat law”  $dS = (dE + PdV)/T$  ?)

## Tentative Fourth Laws or Principles

Most variations of hypothetical fourth laws (or principles) have to do with the environmental sciences, biological evolution, or galactic phenomena. Most fourth law statements, however, are speculative and far from agreed upon. The most common proposed Fourth Law is the **Onsager reciprocal relations**. Another example is the maximum power principle as put forward initially by biologist Alfred Lotka in his 1922 article Contributions to the Energetics of Evolution.

## Statistical Relations and Postulate

- $S = k \ln \Omega$
- $P \propto \Omega \propto e^{S/k}$

- Equal a priori probability postulate: Given an isolated system in equilibrium, it is found with equal probability in each of its accessible microstates. (or thermodynamic postulate?)

## Fundamental Relations for common Thermodynamic Potentials

(“pre-Maxwellian Relations”) (partial Legendre Transforms of  $E$ ; of  $S \Rightarrow$  Massieu functions)

- In general,  $dU = -\sum_{k=0}^t P_k dX_k = TdS - \sum_{k=1}^t P_k dX_k$   
Or  $dU = -\sum_{m=0, k=0}^{r,t} P_{m,k} dX_{m,k}$  for  $r$ -component systems and  $t$  force/displacement conjugate pairs

$$\cdot E = F + TS = H - PV = G + TS - PV$$

$$\cdot F \equiv E - TS = H - TS - PV = G - PV$$

$$\cdot H \equiv E + PV = F + TS + PV = G + TS$$

$$\cdot G \equiv E - TS + PV = F + PV = H - TS$$

- $dE = TdS - PdV \quad T = \left(\frac{\partial E}{\partial S}\right)_V \quad -P = \left(\frac{\partial E}{\partial V}\right)_S$

- $dF = -SdT - PdV \quad -S = \left(\frac{\partial F}{\partial T}\right)_V \quad -P = \left(\frac{\partial F}{\partial V}\right)_T$

- $dH = TdS + VdP \quad T = \left(\frac{\partial H}{\partial S}\right)_P \quad V = \left(\frac{\partial H}{\partial P}\right)_S$

- $dG = -SdT + VdP \quad -S = \left(\frac{\partial G}{\partial T}\right)_P \quad V = \left(\frac{\partial G}{\partial P}\right)_T$

Don't forget to list the assumptions used here!

- Hey, should the Gibbs-Duhem relation go here?

## Maxwell Relations

- $\frac{\partial^2 E}{\partial V \partial S} = \frac{\partial^2 E}{\partial S \partial V} \Rightarrow \left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V$

- $\frac{\partial^2 F}{\partial T \partial V} = \frac{\partial^2 F}{\partial V \partial T} \Rightarrow -\left(\frac{\partial S}{\partial V}\right)_T = -\left(\frac{\partial P}{\partial T}\right)_V$

- $\frac{\partial^2 H}{\partial S \partial P} = \frac{\partial^2 H}{\partial P \partial S} \Rightarrow \left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P$

- $\frac{\partial^2 G}{\partial T \partial P} = \frac{\partial^2 G}{\partial P \partial T} \Rightarrow -\left(\frac{\partial S}{\partial P}\right)_T = \left(\frac{\partial V}{\partial T}\right)_P$

## Further Relations Derived from Maxwell Relations

- The Granddaddy of Relations:  $\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V - P$  (Why did Putterman call it that?)

- Fluctuations from equilibrium:

Say a variable  $y$  is fluctuating about the equil value  $\tilde{y}$ . Given that  $\frac{\mathcal{P}(y)}{\mathcal{P}_{\max}} = e^{(S(y)-S_{\max})/k_B}$ , using a Taylor expansion of  $S(y)$  about  $S(\tilde{y}) = S_{\max}$ , and assuming the third- and higher-order partial-derivative-of- $S$ -wrt- $y$  terms are negligible, we find that the fluctuations are described by a Gaussian distribution with dispersion

$$\langle (y - \tilde{y})^2 \rangle = k_B \left| \partial^2 S / \partial y^2 (\tilde{y}) \right|^{-1}$$

## More Fundamental Relations

Gibb's free energy  $G$ ; "this is the thermodynamic potential that depends on magnetization  $M$  and temperature  $T$ " (Peskin pg 269)  $H$  is the external magnetic field.

$$\left(\frac{\partial G}{\partial M}\right)_T = H$$

## 7 People and Old Eponymous Laws

See [http://en.wikipedia.org/wiki/Scientific\\_laws\\_named\\_after\\_people](http://en.wikipedia.org/wiki/Scientific_laws_named_after_people)

- Antoine-Laurent de Lavoisier, Nicolas Léonard Sadi Carnot, Robert Boyle, Jacques Charles, Joseph Louis Gay-Lussac, John Dalton, Amedeo Avagadro, Benoit Paul Émile Clapyron, Rudolf Claussius, Josiah Willard Gibbs, Pierre Duhem, Henri-Louis Le Chatelier
- Lavoisier
- (1662) **Boyle's Law**

$$PV = \text{const.}$$

- (1787) **Charles's Law** or Law of Charles and Gay-Lussac

$$\frac{V}{T} = \text{const.} \quad \text{or} \quad \frac{V_1}{T_1} = \frac{V_2}{T_2}$$

- (1801) **Dalton's Law** of Partial Pressures

$$P_{\text{total}} = \sum_{i=1}^n p_i$$

...related to ideal gas law...

- **Gay-Lussac's Law(s)**

1. (1802) The pressure of a fixed amount of gas at fixed volume is directly proportional to its temperature in kelvins:

$$\frac{P}{T} = \text{const.} \quad \text{or} \quad \frac{P_1}{T_1} = \frac{P_2}{T_2}$$

for the same substance under two different sets of conditions  $(P_1, T_1)$  and  $(P_2, T_2)$ .

2. (1809) The ratio between the combining volumes of gases and the product, if gaseous, can be expressed in small whole numbers.

- (date?) **Combined Gas Law** ( $\Leftarrow$  Gay-Lussac [1] + Charles's + Boyle's Laws)

$$\frac{PV}{T} = \text{const.} \quad \text{or} \quad \frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$$

- (1811) **Avagadro's Law**

Equal volumes of gases, at the same temperature and pressure, contain the same number of particles or molecules:

$$\frac{V}{N} = a \quad \text{or} \quad \frac{V(T, P)}{N} = a(T, P)?$$

where  $V$  is the volume of any gas at a particular temperature  $T$  and pressure  $P$ ,  $N$  is the number of

particles or molecules, and  $a$  is a constant (that depends on the temperature and pressure?)

Thus, the number of molecules in a specific volume of gas is independent of the size or mass of the gas molecules.

The most important consequence of Avogadro's law is the following: The ideal gas constant has the same value for all gases. This means that the constant:

$$\frac{P_1 V_1}{T_1 n_1} = \frac{P_2 V_2}{T_2 n_2} = \text{const.}$$

- (1834) **Ideal Gas Law** ( $\Leftarrow$  Combined Gas + Avogadro's Laws) (Émile Clapeyron)

The equation of state of a hypothetical ideal gas.  $PV_m = R[T_C + (273.15 \text{ }^\circ\text{C})]$

$$PV = nRT$$

- (1843) **Carnot's Principle**: (Carnot cycle, Clausius Theorem?) Clapeyron made a definitive statement of Carnot's principle, what is now known as the second law of thermodynamics.
- (1888) **Le Chatelier's Principle** (?): the response of a chemical system perturbed from equilibrium will be to counteract the perturbation.
- **Clausius-Clapeyron Relation**

The Clausius-Clapeyron relation gives the slope of the coexistence curve (the line separating two phases in a  $P$ - $T$  diagram) and characterizes phase transitions:

$$\frac{dP}{dT} = \frac{L}{T\Delta V}$$

where  $L$  is the latent heat.

Derivation: use chemical potentials, Gibbs-Duhem relation, and the second law (b).

- Others: (1880) Amagat's Law of Partial Volumes, Raoult's Law and Henry's Law (re: partial vapor pressures of ideal solutions and concentrations of solute)

## 8 Theorems, Postulates, Hypotheses, and Demons

- **Fundamental Thermodynamic Postulate**: An isolated system in equilibrium is equally likely to be in any of its accessible states. (or statistical postulate?)
- **Liouville Theorem** and Equation (from classical mechanics)  
Applies to quasi-closed subsystems and is thus only valid for not-too long intervals of time, during which the subsystem behaves as if closed, to a sufficient approximation. The distribution function is constant along the phase trajectories of the subsystem. (Landau pg 10)  
A consequence of Liouville's theorem: "if one considers a representative ensemble of ... isolated systems where these systems are distributed uniformly (i.e., with equal probability) over all their accessible states at any one time, then they will remain uniformly distributed over these states forever." (Reif pg 54)
- **Fluctuation Theorem**  
The Liouville equation is integral to the proof of the fluctuation theorem from which the second law of thermodynamics can be derived.
- **Clausius Theorem** (Carnot cycle, Carnot principle?)

- Lemma: Any reversible process can be replaced by a combination of reversible isothermal and adiabatic processes.
- **Helmholtz Theorem** (of classical mechanics)
- **Ergodic Hypothesis**
- **Generalized Helmholtz Theorem**  
A multidimensional version of the Helmholtz theorem, based on the ergodic theorem of George David Birkhoff.
- (1872) **H-Theorem** (regarding entropy) and the approach to equilibrium  
(1876) Loschmidt's paradox  
Quantum mechanical H-theorem  
1872 - Ludwig Boltzmann states the Boltzmann equation for the temporal development of distribution functions in phase space, and publishes his H-theorem  
1876 - Johann Loschmidt criticises Boltzmann's H theorem as being incompatible with microscopic reversibility (Loschmidt's paradox).
- **Equipartition Theorem** (classical statistical mechanics)
- **Euler's Theorem** for homogeneous functions
- **Nernst Postulate**
- **Gibbs Phase Rule**  
 $i$ , Number of independent intensive variables (Number of degrees of freedom  $f = i$ ) (really?);  $s$ , Number of chemical species;  $p$ , Number of phases;  $r$ , Number of independent reactions;  $c$ , Number of components ( $c = n - r$ )  
 $i = s - r - p + 2 = c - p + 2$  if chemical reactions are involved  
 $i = s - p + 2$  The Gibbs-Duhem equation can be regarded as the source of the phase rule, for a system involving only PV work and chemical work, but no chemical reactions.  
 $i = s + 1$  for a one-phase system
- Natural Variables, number of potentials, etc.  
 $v$ , Number of natural variables (independent variables to describe the extensive state);  $f$  Number of degrees of freedom ( $f = i$ )  
 $v = i + p = s - r + 2 = c + 2$  for a system with chemical reactions  
 $v = i + p = s + 2$  for a system without chemical reactions  
 $2^v - 1$ , Number of Legendre transforms (non-zero ones?)  
 $2^v$ , Number of thermodynamic potentials for a system  
( $2^v$  includes the potential that is equal to zero and yields the Gibbs-Duhem equation)  
 $v(v - 1)/2$ , Number of Maxwell equations for each of the thermodynamic potentials  
 $[v(v - 1)/2]2^v$ , Number of Maxwell equations for all of the thermodynamic potentials for a system  
When Legendre transforms are used to introduce two new natural variables ( $T, P$ ), then  $2^v = 2^2 = 4$  thermodynamic potentials are related by Legendre transforms, as we have seen with  $U, H, A$ , and  $G$ . There are four Maxwell equations.  
Intensive variables are introduced as natural variables only by use of Legendre transforms. Since a Legendre transform defines a new thermodynamic potential, it is important that the new thermodynamic property have its own symbol and name. The new thermodynamic potentials contain all

the information in  $U(S, V\{n_i\})$ , and so the use of  $U$ ,  $H$ ,  $A$ ,  $G$ , or other thermodynamic potential in place of  $U$  is simply a matter of convenience.

- **Maxwell's Demon**
- **Laplace's Demon**

## 8.1 Proving Theorems

- Virial theorem + Equipartition theorem  $\Rightarrow$  Ideal Gas Law
- Virial theorem + (?)  $\Rightarrow$  equations of state for imperfect or nonideal gases

## 9 Important Physical Systems, Phenomena, and Applications

- Inelastic collisions

The importance of inelastic collisions of the first and second kinds for reaching equilibrium.

- 1st Kind: An inelastic collision in which some of the kinetic energy of translational motion is converted to internal energy of the colliding systems. A.k.a. an endoergic collision.
- 2nd Kind: An inelastic collision in which some of the internal energy of the colliding systems is converted to kinetic energy of translation. A.k.a. an exoergic or “super-elastic” collision.

- Ideal Gas

(Departure function)

- Chemistry

electrochemical cell, chemical reactions, chemical thermodynamics, Nernst equation, activation energy, Arrhenius equation

- Black-Body Radiation

- Some History

- \* 1791 - Pierre Prévost shows that all bodies radiate heat, no matter how hot or cold they are
- \* 1804 - Sir John Leslie observes that a matte black surface radiates heat more effectively (i.e., loses energy more quickly due to radiation) than a polished surface, suggesting the importance of black-body radiation
- \* 1831 - Macedonio Melloni demonstrates that black-body radiation can be reflected, refracted, and polarised in the same way as light
- \* 1859 - Gustav Kirchoff shows that energy emission from a black body is a function of only temperature and frequency (he introduces the term “black body” in 1862)
- \* 1879 - Jožef Stefan observes that the total radiant flux from a black body is proportional to the fourth power of its temperature and states the Stefan-Boltzmann law.
- \* 1884 - Boltzmann derives the Stefan-Boltzmann black-body radiant flux law from thermodynamic and electrodynamic considerations.
- \* 1893 - Wilhelm Wien discovers the displacement law for a blackbody's maximum specific intensity.

- Energy emission from a black body is a function of only temperature and frequency (and emission angle, since a black body is a Lambertian radiator).
- perfect absorber and “perfect emitter” (I think black-bodies are defined to be “perfect” emitters, because their emission spectra are mathematical envelopes for all other emission by bodies: they

have an emissivity of  $\epsilon = 1$ )

- emissivity: ratio of energy radiated by the material to energy radiated by a black body at the same temperature. (specific emissivity? depends on temperature, frequency/wavelength, emission angle)
- absorptivity
- All bodies radiate, whatever their temperature. **Kirchhoff's Law of thermal radiation:** At thermal equilibrium, emissivity equals absorptivity for all bodies.
- Grey body, brown body
- Engines
  - Carnot Cycle
- Superconductivity
- Magnetic cooling
- Bose-Einstein condensate
- Fermion condensate (Advanced?)
- (Reif Ch 12,13: scattering, thermal conductivity, electrical conductivity, viscosity)
- Solar Spectrum: absorption lines and other deviations from the black-body spectrum (why should it emit like a black body in the first place?)
  - Inelastic collisions of the second kind
  - Thermal doppler shifting
  - Bremsstrahlung radiation from collisions
  - Surface of last scattering for different frequencies is at different elevations and temperatures
  - The “wings ” on the absorption line (or dip) are caused by uncertainty in the energy (frequency) of the photons, since they are released by atoms and molecules that only briefly occupy excited states
- Joule-Thomson process / effect / (expansion?) (Throttling) (or Joule-Kelvin)  
the change in temperature that accompanies expansion of a gas without production of work or transfer of heat. At ordinary temperatures and pressures, all real gases except hydrogen and helium cool upon such expansion; this phenomenon often is utilized in liquefying gases
- Joule expansion
- Entropy of a gravitationally collapsing gas (Seemingly defies 2nd law of thermo)  
See <http://math.ucr.edu/home/baez/entropy.html>

## 10 Models, Paradoxes, and Catastrophes

- **Ideal Gas**

- **van der Waals Gas**

- **Molecular gas**

line Virial Expansion of the equation of state

$$\frac{p}{kT} = n + B_2(T) n^2 + B(T) n^3 + \dots$$

Virial coefficients:  $B_1(T) = 1$ ,  $B_2(T)$ ,  $B_3(T)$ , ...

$$B_2(T) = -2\pi \int_0^\infty (e^{-\beta u} - 1) R^2 dR \text{ where } u \text{ is the intermolecular potential}$$

- **Black-body Radiation**

Radiation of a black-body in thermal equilibrium.

Black-body energy flux density (or intensity, power area-density, radiant flux, emissive power, irradiance), in terms of intensity frequency-solid-angle-density and intensity wavelength-solid-angle-density:

$$s = I = \int i(\nu, T) d\nu d\Omega = \int i(\lambda, T) d\lambda d\Omega$$

“Energy density distribution”:  $u(\nu, T)$  (see if the equations using this below are in a good unit system)

- (1879) **Stefan-Boltzmann Law** (a.k.a. Stefan’s Law)

Black-body energy flux density:

$$s = \epsilon \sigma T^4$$

where  $\epsilon$  is the black-body’s emissivity ( $\epsilon = 1$  for a perfect black-body) and the Stefan-Boltzmann constant (or Stefan’s constant)  $\sigma = (5.670\,400 \times 10^{-8} \text{ Wm}^{-2}\text{K}^{-4})$ . Using Planck’s Law, one can derive that  $\sigma = 2\pi^5 k^4 / 15c^2 h^3$ . ( $\sigma = 8\pi^5 k^4 / 15h^3 c^3$ ?)

The law was discovered experimentally by Jožev Stefan in 1879. The proportionality was derived theoretically, using thermodynamics and Maxwell’s electrodynamics, by Ludwig Boltzmann in 1884. (Or was the law, including the proportionality, derived in 1884?)

- (1893) **Wien’s Displacement Law**

$$\lambda_{\text{peak}} = \frac{b}{T} \quad \text{or} \quad \nu_{\text{peak}} = \frac{c}{\lambda_{\text{peak}}} = \frac{4.96}{h} kT$$

where Wien’s displacement constant  $b = (2.897\,768\,5(51) \times 10^{-3} \text{ m} \cdot \text{K})$ . (Using Planck’s Law, one can derive that  $b = hc/kx$  where  $x$  is the solution to  $x/(1 - e^{-x}) = 5$ :  $x = 4.965\,114\,231\,744\dots$ ) ( $x = 4.9663$ ?)

Wien formulated his law based on empirical data.

- (1894) **Wien’s Distribution Law** (a.k.a. Wien’s Approximation) (1894 or 1896?)

Energy density distribution:

$$u(\nu, T) = A\nu^3 e^{-\gamma\nu/T}$$

where  $A$  and  $\gamma$  are two parameters that can be adjusted to fit experimental data.

Wien derived this using the Stefan-Boltzmann law and thermodynamical arguments.

$$i(\nu, T) = \frac{2h\nu^3}{c^2} e^{-h\nu/kT} \quad \text{or} \quad i(\lambda, T) = \frac{2hc^2}{\lambda^5} e^{-hc/\lambda kT} (?)$$

- (1900) **Rayleigh-Jeans Law**

Energy density:

$$f(\lambda, T) = 8\pi \frac{kT}{\lambda^4} \quad (1905)$$

$$f(\lambda, T) \propto \frac{T}{\lambda^4} \quad (1900)$$

$$u(\nu, T) = \frac{8\pi\nu^2}{c^3} kT$$

Derived using thermodynamics and electrodynamics by Rayleigh in 1900 with these steps: assume the radiation exists in standing E&M waves, then the energy density is the product of the number

of modes of oscillation per unit volume per unit frequency and the average energy per mode (which is independent of frequency)

$$u(\nu, T) = N(\nu) \langle E \rangle = \frac{8\pi\nu^2}{c^3} \frac{\int_0^\infty E e^{-E/kT} dE}{\int_0^\infty e^{-E/kT} dE} = \frac{8\pi\nu^2}{c^3} kT,$$

by the equipartition theorem.

(Lord Rayleigh derived the proportionality relation in 1900, while Sir James Jeans derived the proportionality constant in 1905.)

- (1901) **Planck's Law** of black-body radiation (a.k.a. Wien-Planck Law)

$$u(\nu, T) = \frac{8\pi\nu^2}{c^3} \frac{h\nu}{e^{h\nu/kT} - 1}$$

Planck's quantization rule, or postulate, was that the energy emitted by the oscillating charges in the wall of the cavity must be integer multiples of  $h\nu$  ( $E = nh\nu$ ) so the average energy per mode or oscillator must be a sum rather than an integral:

$$\langle E \rangle = \frac{\sum_{n=0}^{\infty} nh\nu e^{-nh\nu/kT}}{\sum_{n=0}^{\infty} e^{-nh\nu/kT}} = \frac{h\nu}{e^{h\nu/kT} - 1}$$

which is independent of frequency.

$$i(\nu, T) = \frac{2h\nu^3}{c^2} \frac{1}{e^{h\nu/kT} - 1} \quad \text{or} \quad i(\lambda, T) = \frac{2hc^2}{\lambda^5} \frac{1}{e^{hc/\lambda kT} - 1} (?)$$

$$f(\lambda, T) = \frac{8\pi hc}{\lambda^5} \frac{1}{e^{hc/\lambda kT} - 1}$$

- **Ultraviolet Catastrophe** (or Rayleigh-Jeans Catastrophe)

Term "UV catastrophe" coined in 1911 by Paul Ehrenfest. (Ultraviolet is merely referring to high frequency electromagnetic radiation, which includes x-rays, gamma rays, and the whole upper spectrum. On an intensity-frequency plot, there is no spike or divergence within the UV window of the spectrum; however, on an intensity-wavelength plot, the curve diverges as wavelength vanishes.)

(energy density diverges or goes to infinity as frequency goes to infinity, and thus total energy diverges)

Planck did not consider the equipartition theorem to be universally valid, so he never noticed any sort of "catastrophe" - it was only discovered some five years later by Einstein, Lord Rayleigh, and Sir James Jeans.

- **Specific Heat** (or specific heat capacity) of Solid Bodies and Gases

1819 - Pierre Louis Dulong and Alexis Thérèse Petit give the Dulong-Petit law for the specific heat capacity of a crystal

"As far as the specific heat of solid bodies is concerned, Einstein's theory, which rested upon the assumption of a single natural vibration of the atom, was extended by M. Born and Th. von Krmn to the case of various kinds of natural vibrations, which approached more nearly to the truth. P. Debye succeeded, by means of a bold simplification of the stipulations for the character of natural vibrations, in producing a relatively simple formula for the specific heat of solid bodies which, particularly for low temperatures, not only satisfactorily reproduces the measurements obtained by W. Nernst and his pupils, but is also compatible with the elastic and optical properties of these substances. The

quantum of action also comes to the fore in considering the specific heat of gases. W. Nernst had earlier suggested that to the quantum of energy of a vibration there must also correspond a quantum of energy of a rotation, and accordingly it was to be expected that the rotational energy of the gas molecules would disappear with falling temperature. The measurements by A. Eucken on the specific heat of hydrogen confirmed this conclusion, and if the calculations of A. Einstein and O. Stern, P. Ehrenfest and others have not until now afforded any completely satisfactory agreement, this lies understandably in our, as yet, incomplete knowledge of the model of a hydrogen molecule. The fact that the rotations of the gas molecules, as specified by quantum conditions, do really exist in Nature, can no longer be doubted in view of the work on absorption bands in the infrared by N. Bjerrum, E. von Bahr, H. Rubens, G. Hetmer and others, even though it has not been possible to give an all-round exhaustive explanation of this remarkable rotation spectra up to now.” – Planck [3] 1920

– **Debye model** of solids, (specific) heat capacity

In 1912, Debye extended Albert Einstein’s theory of specific heat to lower temperatures by including contributions from low-frequency phonons.

How much of this is important to know? ...

Debye frequency:  $\omega_D = c_s \left(6\pi^2 \frac{N}{V}\right)^{1/2}$

Debye function:  $f_D(y)$

Debye temperature:  $\theta_D$

Debye approximation

$$C_V = \frac{12\pi^4}{5} Nk \left(\frac{T}{\theta_D}\right)^3$$

– **Einstein model** of solids, heat capacity

• **Gibbs Paradox** (→ Sackur-Tetrode equation)

• **Ising Model**, Potts Model, Etc.

• **Mean Field Theory**

Bogoliubov inequality

Reif pg 430: Weiss molecular-field theory, approximation, Brillouin function, (critical temperature...)

Curie temperature (pg 432), (general consistency condition, pg 433)

• ...

## 11 Advanced or Additional Topics, (Beyond These Notes?)

• Random Processes

– Brownian motion

– Langevin, Fokker-Planck equations (nonequilibrium)

• **Nonequilibrium Statistical Mechanics**

Liouville’s Thm, Boltzmann Eqn (far from equilibrium, transport quantities) [collisionless Boltzmann Eqn called Liouville Eqn or Vlasov Eqn],

• Phase transitions

– (First-Order phase transition)

– Second-Order phase transition (critical point), Landau theory, (QFT, field mass  $\rightarrow 0$  at phase transition; Peskin pg 268-9)

• Boltzmann Equation

- 1948 - Claude Elwood Shannon establishes information theory. (information entropy here?)
- 1957 - Edwin T. Jaynes gives MaxEnt interpretation of thermodynamics from information theory.
- 1972 - Jacob Bekenstein suggests that black holes have an entropy proportional to their surface area.
- 1974 - Stephen Hawking predicts that black holes will radiate particles with a black-body spectrum which can cause black hole evaporation

## 12 Open Questions and Mysteries

- Theory of melting
- Theory of the speed of sound
- (Complete model for the creation of the magnetic field of the Earth?)

## 13 Constants and Important Quantities

Name of Constant	Symbol	Value
Boltzmann constant	$k$ (oftentimes written elsewhere as $k$ or $k_B$ )	$1.38 \times 10^{-23}$ J/K
Electrostatic (Coulomb) constant	$K_e$ (oftentimes written elsewhere as $k$ or $k_C$ )	$8.99 \times 10^9$ Nm <sup>2</sup> /C <sup>2</sup>
(universal or ideal) gas constant	$R$	$8.314$ JK <sup>-1</sup> mol <sup>-1</sup>

## 14 Problem-Solving Issues

- When you are asked to “write down *the* fundamental thermodynamic relation” for a particular system, this is (or should be) different than being asked to “write down *a* fundamental thermodynamic relation” for that system. In the first case, you should write down the fundamental relation of thermodynamics,

$$dE = TdS - PdV \quad \text{or} \quad dE = \delta Q - \delta W ?$$

and then solve for and substitute the appropriate quantities (e.g., ..., or...). In the second case, you should

## References

- [1] Herbert B. Callen: *Thermodynamics and an Introduction to Thermostatistics, Second Edition*, John Wiley & Sons (1985)
- [2] F. Reif: *Fundamentals of Statistical and Thermal Physics*, McGraw-Hill (1965)
- [3] Max Planck: “The Genesis and Present State of Development of the Quantum Theory,” from *Nobel Lectures, Physics 1901-1921*, Elsevier Publishing Company, Amsterdam (1967). Available at <[http://nobelprize.org/nobel\\_prizes/physics/laureates/1918/planck-lecture.html](http://nobelprize.org/nobel_prizes/physics/laureates/1918/planck-lecture.html)> (Accessed January 2007).
- [4] Herbert Goldstien: *Classical Mechanics, Second Edition*, Addison-Wesley (1980)
- [5] Robert A. Alberty: “Use of Legendre Transforms in Chemical Thermodynamics,” International Union of Pure and Applied Chemistry (IUPAC) Technical Report (Physical Chemistry Division, Commission on Thermodynamics). Available at <<http://www.iupac.org/publications/pac/2001/pdf/7308x1349.pdf>>.