

# Chapter 1

## Thermodynamics<sup>1</sup>: review and background

### 1.1 Thermodynamics: a phenomenological description of equilibrium properties of macroscopic systems

“Suppose you’ve got theoretical physics cracked. Suppose you know all the fundamental laws of Nature, the properties of the elementary particles and the forces at play between them. How can you turn this knowledge into an understanding of the world around us? More concretely, if I give you a box containing  $10^{23}$  particles and tell you their mass, their charge, their interactions, and so on, what can you tell me about the stuff in the box?

There’s one strategy that definitely won’t work: writing down the Schrödinger equation for  $10^{23}$  particles and solving it. That’s typically not possible for 23 particles, let alone  $10^{23}$ . What’s more, even if you could find the wavefunction of the system, what would you do with it? The positions of individual particles are of little interest to anyone. We want answers to much more basic, almost childish, questions about the contents of the box. Is it wet? Is it hot? What colour is it? Is the box in danger of exploding? What happens if we squeeze it, pull it, heat it up? How can we begin to answer these kind of questions starting from the fundamental laws of physics?

The purpose of this course is to introduce the dictionary that allows you translate from the microscopic world where the laws of Nature are written to the everyday macroscopic world that we’re familiar with. This will allow us to begin to address very basic questions about how matter behaves.” – David Tong, *Lecture notes on Statistical Physics*

We begin with a few phenomenological definitions:

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<sup>1</sup>“Thermodynamics is a funny subject. The first time you go through it, you don’t understand it at all. The second time you go through it, you think you understand it, except for one or two small points. The third time you go through it, you know you don’t understand it, but by that time you are used to it, so it doesn’t bother you any more.” – Arnold Sommerfeld, As quoted in: J.Muller, *Physical Chemistry in Depth* (Springer Science and Business Media, 1992)

As phenomenology, it is based on empirical observations, summarized by the laws of thermodynamics; a consistent mathematical framework is then built on top of these observations.

## Closed system

We will think about isolating a system thermally by “adiabatic walls” that do not allow heat exchange with the outside world. This is like a “point particle” approximation. We will sometimes consider “diathermic walls” which do allow such exchange of heat.

## Equilibrium

A state in which “properties” don’t change over the *period of observation* – this dependence on observation time makes the definition a *subjective* one. You observe that you do something, the system goes through some transient behavior, and then settles down into a state which seems not to change.

## Macroscopic properties

The systems under study will be characterized by *thermodynamic coordinates* or *state functions*, such as *mechanical* properties:  $(V, P)_{\text{gas}}$ , or  $(L, F)_{\text{wire}}$ , or  $(M, B)_{\text{magnet}}$ , etc..., *plus some thermal properties*.

**Phenomenology:** How do these thermodynamic coordinates depend on each other, or co-evolve? Rely on empirical observations and from them construct laws of thermodynamics.

## 1.2 0<sup>th</sup> Law

The zeroth law is a statement of the transitivity of (thermal) equilibrium:

### Observation

*If two systems, A and B, are separately in equilibrium with system C, then they are in equilibrium with each other*

Note that this implies the existence of “Temperature,” some additional thermodynamic coordinate, we can use to describe a system.

### Implications

We describe the state of each system,  $A$ ,  $B$ , and  $C$ , by a set of thermodynamic coordinates, e.g.  $\{A_1, A_2, \dots\}$ . The statement “ $A$  and  $C$  are in equilibrium” can be expressed by a constraint between these coordinates **that is, a change in  $A_1$  must be accompanied by some changes in  $\{A_2, \dots, C_1, C_2, \dots\}$  to maintain the equilibrium between the states.** There should be an additional coordinate (i.e., on top of the mechanical thermodynamic coordinates) to

describe the system... we'll call that coordinate "temperature". Let's write that constraint via a function; what follows is physicists' math... hand-waving ensues.

$$f_{AC}(A_1, \dots, C_1 \dots) = 0. \quad (1.1)$$

Likewise

$$f_{BC}(B_1, \dots, C_1 \dots) = 0. \quad (1.2)$$

Each of the above can be, in general, written as a constraint on one of the coordinates of  $C$ :

$$F_{AC}(A_1, \dots, C_2 \dots) = C_1 = F_{BC}(B_1, \dots, C_2 \dots). \quad (1.3)$$

Is it obvious we can even *do* this, mathematically (i.e., go from Eq. 1.1 to 1.3)? No. But physically, yes.

The above is a statement about the first ("if") clause of the zeroth law. Great. But the zeroth law says that  $A$  and  $B$  are *also* in equilibrium, so there is some function

$$f_{AB}(A_1, \dots, B_1 \dots) = 0. \quad (1.4)$$

Furthermore, it must be possible to simplify Eq. 1.3 by cancelling the coordinates of system  $C$ . Thus,

$$F_A(A_1, \dots) - F_B(B_1 \dots) = 0. \quad (1.5)$$

We'll denote this function, the *empirical temperature* by  $\Theta$ , so

$$\Theta_A(A_1, \dots) = \Theta_B(B_1 \dots). \quad (1.6)$$

Thus: equilibrium of systems can be cast as a function that depends only on the coordinates of one of the systems. Draw isotherm of ideal gas?

One can also say something along the lines of "The zeroth law is like an equivalence relation between mathematical sets – the equivalence relation partitions the space of all possible thermodynamic coordinates into mutually distinct subsets; let's *label* those subsets by something, and we'll call that something "temperature."

## Ideal gas scale

The zeroth law states the existence of isotherms: e.g.,  $\Theta_A(A_1, \dots) = \Theta$  Think of, e.g., ideal gas law, or Curie paramagnet, or Hooke's law for rubbers, or van der Waals gases, or.... To construct an actual temperature scale we need a well-defined reference systems. Empirical observation: the product of pressure times volume is constant along the isotherms of any gas that is sufficiently dilute. Think of, e.g., a piston in the ocean or something The ideal gas refers to the dilute limit of real gases (i.e., in the  $P \rightarrow 0$  or  $V \rightarrow \infty$  limits), and the constant of proportionality is determined by reference to the triple point of the ice-water-steam system, which was defined as 273.16°K By the 10th General Conference on Weights and Measures, 1954. Revisions in 1990? .

So define an empirical temperature by using a dilute gas as a thermometer:

$$T(^{\circ}K) \equiv 273.16 \left( \lim_{P \rightarrow 0} (PV)_{\text{system}} \right) / \left( \lim_{P \rightarrow 0} (PV)_{\text{ice-water-steam}} \right) \quad (1.7)$$

## 1.3 1<sup>st</sup> Law

The first law is a statement about the conservation of energy, adapted for thermal systems. We'll formulate it as:

### Statement

*If the state of an adiabatically isolated system is changed by work, the amount of work is only a function of the initial and final coordinates of the system. Draw, fake system with a spring, magnet, etc., a coordinate space representation with initial and final points, and many paths between them.  $\Delta W$  doesn't depend on path*

### Consequences

We infer the existence of *another* state function, the internal energy  $E(\mathbf{X})$ . Think about how the path-independence of the work we have to do when pushing a ball up a frictionless hill in classical mechanics lets us deduce a potential energy.

$$\Delta W = E(\mathbf{X}_f) - E(\mathbf{X}_i) \quad (1.8)$$

Similarly, in the same sense that the zeroth law let us construct some function of coordinates that was relevant to equilibrium, the first law allows us to define another function, the internal energy.

Draw some squiggly paths on the board.

The real content of the first law is when we violate the condition. That is, allow walls that permit heat exchange, so that  $\Delta W \neq E_f - E_i$ . We, of course, still believe energy is a good, conserved quantity, so define *heat*:

$$\Delta Q = (E_f - E_i) - \Delta W. \quad (1.9)$$

Clearly, though,  $\Delta Q$  and  $\Delta W$  are not separate functions of state, so we will use notation like:

$$dE(\mathbf{X}) = dQ + dW, \quad (1.10)$$

Where  $d$  means a differential where the thing is a function of state, and  $d$  means that the thing is path-dependent. Note the sign convention, here, where work and heat *add* energy to the system.

### Quasi-static transformation

A QS transformation is one which is done sufficiently slowly enough to maintain the system in equilibrium everywhere along the path. For such a transformation the work done *on* the system can thus be related to changes in the thermodynamic coordinates. Let's divide the state functions,  $\mathbf{X}$ , into *generalized displacements*  $\mathbf{x}$  and *generalized forces*  $\mathbf{J}$ . Then, in a QS transformation

$$dW = \sum_i J_i dx_i \quad (1.11)$$

## Common generalized coordinates

System	generalized force		generalized displacement	
Wire	tension	$F$	length	$L$
Film	surface tension	$\sigma$	area	$A$
Fluid	pressure	$-P$	volume	$V$
Magnet	field	$B$	magnetization	$M$

Note that the *displacements are generally extensive* and the *forces are generally intensive*.

Question: We've written

$$dE = \sum_i J_i dx_i + \boxed{?} \quad (1.12)$$

What is  $dQ$ ? probably depends on  $T$ . What is it conjugate to?

## Response functions

The usual way of characterizing the behavior of a system (measured from changes in thermodynamic coordinates with external probes). E.g.:

**Force constants** Measure the ratio of displacements to forces (think spring constants). For example, *isothermal compressibility of a gas*:  $\kappa_T = \frac{1}{V} \frac{\partial V}{\partial P} \Big|_T$

**Thermal response** Response to change in temperature, such as the expansivity of a gas  $\alpha_P = \frac{1}{V} \frac{\partial V}{\partial T} \Big|_P$

**Heat capacity** Changes in temperature upon adding heat. **Note that heat is not a state function, so the path is important!** Example: For an ideal gas we could calculate  $C_V = \frac{dQ}{dT} \Big|_V$  and  $C_P = \frac{dQ}{dT} \Big|_P$ , and  $C_P$  has to be bigger since we use some heat to change the volume:

$$\begin{aligned} C_V &= \frac{dQ}{dT} \Big|_V = \frac{dE - dW}{dT} \Big|_V = \frac{dE + PdV}{dT} \Big|_V = \frac{\partial E}{\partial T} \Big|_V. \\ C_P &= \frac{dQ}{dT} \Big|_P = \frac{dE - dW}{dT} \Big|_P = \frac{dE + PdV}{dT} \Big|_P = \frac{\partial E}{\partial T} \Big|_P + P \frac{\partial V}{\partial T} \Big|_P. \end{aligned} \quad (1.13)$$

## Joule's free expansion experiment

Take an adiabatically isolated gas, and let it expand (**adiabatically, but we don't need QS. Draw on the board a two-chambered system**) from  $V_i$  to  $V_f$ . Joule observed that the initial and final temperatures are the same!  $T_f = T_i = T$ .

So,  $\Delta Q = 0$  and  $\Delta W = 0$ , so  $\Delta E = 0$ . We conclude that the internal energy actually depends only on temperature:  $E(P, V, T) = E(T)$ , i.e., a product of  $P$  and  $V$ . Note that since  $E$  depends only on  $T$ ,  $\frac{\partial E}{\partial T} \Big|_V = \frac{\partial E}{\partial T} \Big|_P$ , and we can simplify the heat capacity expressions:

$$C_P - C_V = P \frac{\partial V}{\partial T} \Big|_P = \frac{PV}{T} = Nk_B. \quad (1.14)$$

That last equality is a statement of extensivity, that  $PV/T$  is proportional to an amount of stuff, and  $k_B \approx 1.4 \times 10^{-23} J/K$ .

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## 1.4 2<sup>nd</sup> Law

Why does heat flow from hot to cold? Why are there no perpetual motion machines that work by turning water into ice while doing work? There are many equivalent formulations of the 2nd law; in part because it is fun, we'll see how practical concerns about burning coal to do stuff leads directly to the idea of entropy and its inevitable increase!

### Kelvin's statement

*No process is possible whose sole result is the complete conversion of heat to work ("No ideal engines")*

### Clausius' statement

*No process is possible whose sole result is the transfer of heat from cold to hot ("No ideal refrigerators")*

### Idealized work machines

We'll quantify these statements by defining "figures of merit" for an ideal engine and an ideal refrigerators.

The *efficiency* of an engine, a machine which takes  $Q_H$  of heat from a source, converts some of it to work  $W$ , and dumps some  $Q_C$  of it into a sink, is

$$\eta = \frac{W}{Q_H} = \frac{Q_H - Q_C}{Q_H} \leq 1. \quad (1.15)$$

The *performance* of a refrigerator, an engine running backwards, is

$$\omega = \frac{Q_C}{W} = \frac{Q_C}{Q_H - Q_C} \quad (1.16)$$

Of course, Kelvin and Clausius' formulations are equivalent! To see this, hook up an ideal engine to a fridge, and you get an ideal fridge (so, not Kelvin implies not Clausius). Additionally, run an ideal fridge and take the heat from the exhaust to power an engine and you get an ideal engine (so, not Clausius implies not Kelvin). Thus, Kelvin  $\iff$  Clausius.

This seems trivial; with an excursion through Carnot Engines we'll see that it lets us answer a question posed in section 1.3, when we wrote:

$$dE = \sum_i J_i dx_i + \boxed{?}$$

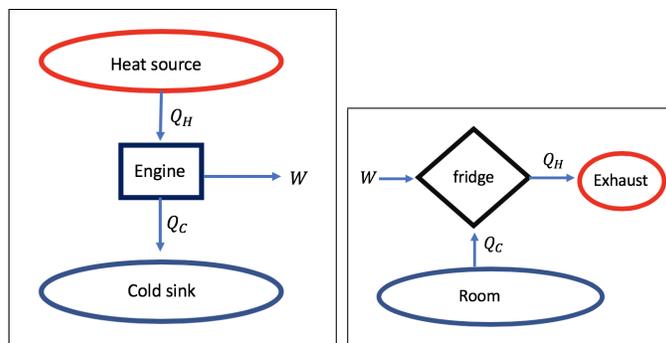


Figure 1.1: **Idealized engine (left) and refrigerators (right)**

## 1.5 Carnot Engines

A *Carnot Engine* (CE) is any engine that (1) is reversible, (2) runs in a cycle, and (3) operates by exchanging heat with a source temperature  $T_H$  and a sink temperature  $T_C$ . Note: (1) is like a generalization of “frictionless” condition in mechanics. Lets us go forward/backward by reversing inputs/outputs. (2) Start and end points are the same. (3) This is more precise than the figure we drew in 1.1; the sinks and sources have well-defined thermodynamic temperatures.

### Ideal gas Carnot Cycle

We know from the 0th law that we can select two ideal-gas isotherms to be the two temperatures. For instance, we could go from  $A$  to  $B$  or from  $C$  to  $D$  in Fig. 1.2 by reversible, adiabatic paths where we maintain the temperature. But how to go *between* the isotherms adiabatically?

For an ideal gas, we know enough to compute the adiabatic curves. Let

$$E = \frac{3}{2}Nk_B T = \frac{3}{2}PV. \quad (1.17)$$

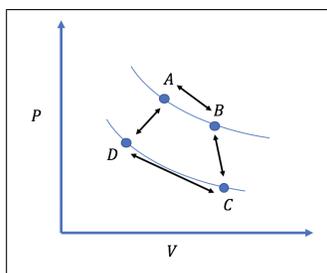


Figure 1.2: **Schematic of a Carnot Cycle for an ideal gas** Note that even schematically there is something obviously wrong with a path drawn here; do you see the error?

Along a quasi-static path we have

$$\begin{aligned} dQ &= 0 = dE - dW = d\left(\frac{3}{2}PV\right) + pdV = \frac{5}{2}PdV + \frac{3}{2}VdP \\ \Rightarrow 0 &= \frac{dP}{P} + \frac{5}{3} \frac{dV}{V} \Rightarrow PV^{5/3} = \text{constant}. \end{aligned} \quad (1.18)$$

It's fun to see (i.e., will probably be a homework problem), that one can construct adiabatics for any two-parameter system with internal energy  $E(J, x)$ .

### Carnot's Theorem

Of all engines operating between  $T_H$  and  $T_C$ , the Carnot engine is the most efficient!

**Proof** Take a Carnot Engine, and use a non-Carnot-Engine's output to run the CE as a refrigerator. Let primes refer to heat connected to the Carnot engine, and unprimes to the NCE. The net effect is to transfer heat  $Q_H - Q'_H = Q_C - Q'_C$  from  $T_H$  to  $T_C$ . Clausius' formulation tells us you can't transfer negative heat, so  $Q_H \geq Q'_H$ . But the amount of work,  $W$ , was the same, so

$$\frac{W}{Q_H} \leq \frac{W}{Q'_H} \Rightarrow \eta_{CE} \geq \eta_{NCE}. \quad (1.19)$$

### 1.5.1 Thermodynamic Temperature Scale

We established (by finding the adiabatic paths) that we can (in theory) construct a Carnot Engine using an ideal gas. All Carnot engines operating between  $T_H$  and  $T_C$  have the same efficiency show by using 1 to run the other backwards, and vice versa, so  $\eta_{CE_1} = \eta_{CE_2}$ . Thus, the efficiency is independent of the engine; it must depend only on the temperatures, i.e. we have  $\eta(T_H, T_C)$ . So, already, *if you can build a CE, it lets us define  $T$  independent of any material properties, just by knowing efficiencies of CE's at different  $T$ .*

We'll make progress by running two engines in series; one between  $T_1$  and  $T_2$ , and the other between  $T_2$  and  $T_3$ , as in Fig. 1.3.

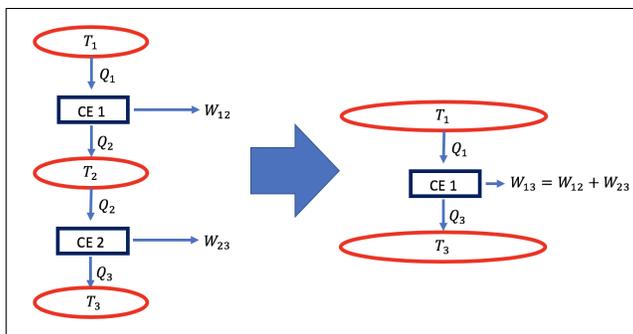


Figure 1.3: Schematic of Carnot engines in series

CE1 tells us

$$Q_2 = Q_1 - W_{12} = Q_1(1 - \eta(T_1, T_2)), \quad (1.20)$$

CE2 tells us

$$Q_3 = Q_2 - W_{23} = Q_2(1 - \eta(T_2, T_3)) = Q_1(1 - \eta(T_1, T_2))(1 - \eta(T_2, T_3)), \quad (1.21)$$

and the combined engine tells us

$$Q_3 = Q_1 - W_{13} = Q_1(1 - \eta(T_1, T_3)). \quad (1.22)$$

Comparing those last two expressions tells us

$$(1 - \eta(T_1, T_3)) = (1 - \eta(T_1, T_2))(1 - \eta(T_2, T_3)), \quad (1.23)$$

which is a constraint on the functional form that  $\eta$  can take. We postulate that

$$(1 - \eta(T_1, T_2)) = \frac{Q_2}{Q_1} \equiv \frac{f(T_2)}{f(T_1)}. \quad (1.24)$$

By convention, let  $f(T) = T$ . Thus

$$\eta(T_H, T_C) = \frac{T_H - T_C}{T_H}. \quad (1.25)$$

We've done it! Up to a constant of proportionality, Eq. 1.25 defines a thermodynamic temperature (and we'll again set the constant using the triple point of water-ice-steam). By running a Carnot cycle for an ideal gas you can show that the ideal gas scale and the thermodynamic temperature scale are identical. This is not useful, but rather conceptual in showing that temperature is not something that depends on the properties of a particular material. Fun note: thermodynamic temperatures must be positive, otherwise Kelvin's Formulation could be violated

## 1.5.2 Clausius' Theorem

### Statement

For any cyclic process, with path parameterized by  $s$

$$\oint \frac{dQ(s)}{T(s)} \leq 0, \quad (1.26)$$

where the heat  $dQ(s)$  is an amount of heat delivered to the system at temperature  $T(s)$  we need not be in equilibrium, so what is  $T(s)$ ? The heat of the "machine" delivering the heat.

### proof

We'll hook up the system to a Carnot engine note that we have not specified the sign of  $dQ$ ; using a Carnot engine and thinking of the cycle as a series of infinitesimal cycles lets us make sure we're delivering whatever  $dQ(s)$  needs to be. Let the Carnot engine be at a given reference temperature  $T_0$ , as in Fig. 1.4A. To prove the theorem, simply reinterpret things by pretending the Carnot engine and the system are a single "device." It looks like

the setup in Fig. fig:clausiusTheoremB. **This looks dumb, but we're done!** To deliver heat at a specified temperature, our efficiency functions from above tell us that  $\bar{d}Q_0 = T_0 \bar{d}Q / T(s)$ . So, From this view the net extracted heat is

$$\oint \bar{d}Q_0(s) = \oint T_0 \frac{\bar{d}Q(s)}{T(s)} \leq 0, \quad (1.27)$$

where the last inequality follows from Kelvin's formulation: We can't only convert  $Q$  to  $W$ !

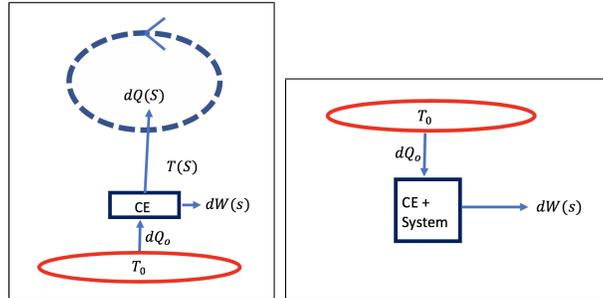


Figure 1.4: **Clausius theorem setup (left) and reinterpretation (right)**

This, as with so much Carnot engine manipulations, feels trivial. There are major consequences!

**1. Entropy!** Let's apply Clausius' Theorem to a **reversible** transformation. Then we have

$$\pm \oint \frac{\bar{d}Q_{rev}(s)}{T(s)} \leq 0. \quad (1.28)$$

Since both the plus and the minus version are less than or equal to zero, the integral vanishes. Now, break the cycle into a path from  $A$  to  $B$  and from  $B$  to  $A$  "the other way." (draw picture). These integrals must be equal:

$$\int_A^B \frac{\bar{d}Q_{rev}^1(s)}{T^1(s)} = \int_A^B \frac{\bar{d}Q_{rev}^2(s)}{T^2(s)}, \quad (1.29)$$

so since the integrals depend only on their endpoints

$$\int_A^B \frac{\bar{d}Q_{rev}(s)}{T(s)} = S_B - S_A, \quad (1.30)$$

where we've just defined a quantity we'll call "entropy"<sup>2</sup> **we have only defined it up to a constant of integration, of course.** For a reversible process we can now compute the heat from  $\bar{d}Q_{rev} = T dS$

<sup>2</sup>"We might call  $S$  the *transformational content* of the body, just as we termed the magnitude  $U$  its *thermal and ergonal content*. But as I hold it to be better to borrow terms for important magnitudes from the ancient languages, so that they may be adopted unchanged in all modern languages, I propose to call the magnitude  $S$  the *entropy* of the body, from the Greek word  $\tau\rho\omicron\pi\eta$ , transformation. I have intentionally formed the word *entropy* so as to be as similar as possible to the word *energy*; for the two magnitudes to be denoted by these words are so nearly allied in their physical meanings, that a certain similarity in designation appears to be desirable." – Clausius, Ninth Memoir, *On several convenient forms of the fundamental equations of the mechanical theory of heat*. For all that talk of borrowing terms for important magnitudes from ancient languages, note that Clausius tried to name the unit of entropy "the Clausius," a calorie per degree Celsius.

**2. The 1st Law, revisited** For a reversible transformation that means we can now write, from  $dE = \bar{d}W + \bar{d}Q_{rev}$ ,

$$dE = \sum_i J_i dx_i + TdS. \quad (1.31)$$

No big deal, just the most important expression in thermodynamics... note we've answered one of our questions: the thing we're calling entropy is an extensive generalized "displacement" with  $T$  as its conjugate generalized force.

**3. Entropy increases for irreversible transformations** Suppose we make an irreversible change as we go from state  $A$  to  $B$ , but then complete the cycle by making a reversible transformation from  $B$  back to  $A$ . Clausius tells us that

$$\int_A^B \frac{\bar{d}Q}{T} + \int_B^A \frac{\bar{d}Q_{rev}}{T} \leq 0 \Rightarrow \int_A^B \frac{\bar{d}Q}{T} \leq S_B - S_A, \quad (1.32)$$

which tells us that, in differential form,  $\bar{d}Q \leq TdS$  for any transformation. For an adiabatic process, with  $\bar{d}Q = 0$ , we've just learned that  $dS \geq 0$ . [As a system approaches equilibrium, apparently the arrow of time points in the direction of increasing entropy, since changes in a system's internal state can only increase  \$S\$ .](#)

**4. How many independent variables do I need to describe an equilibrium system?**

From Eq. 1.31 we see that if there  $n$  ways of doing mechanical work to a system (the  $n$  pairs  $\{J_i, x_i\}$ ), then we need  $n + 1$  independent coordinates to describe equilibrium systems (i.e., if you know  $E$  then then  $J$ 's and  $x$ 's are connected. This gives us freedom we'll exploit later in defining different ensembles, etc. For example, suppose we choose as our coordinates  $E$  and all of the displacements  $x_i$ ; Eq. 1.31 gives us the relations

$$\left. \frac{\partial S}{\partial E} \right|_{\{x_i\}} = \frac{1}{T}, \quad \left. \frac{-\partial S}{\partial x_i} \right|_{\{E, x_{j \neq i}\}} = \frac{J_i}{T}. \quad (1.33)$$


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## 1.6 3<sup>rd</sup> Law

I said last class I wouldn't discuss this next – I've changed my mind, but we'll be very brief! We know from the second law how to compute the difference in entropy between two state points at the same temperature: we make sure we perform operations reversibly, and then calculate  $\Delta S = \int \bar{d}Q_{rev}/T$ .

### 1.6.1 Nernst-Simon statement of the third law

The change in entropy associated with a system undergoing a reversible, isothermal process approaches zero as the temperature approaches 0K:

$$\lim_{T \rightarrow 0} \Delta S(T) \rightarrow 0. \quad (1.34)$$

## Stronger Nernst statement

The entropy of all systems at absolute zero is a universal constant, which we will define to be the zero point of the entropy scale:  $\lim_{T \rightarrow 0} S(\mathbf{X}, T) = 0$ .

### 1.6.2 Consequences

**1. Vanishing of entropy derivatives** Since  $\lim_{T \rightarrow 0} S(\vec{r}_{X,T}) = 0$  for all  $\mathbf{x}$ , we must have that

$$\lim_{T \rightarrow 0} \left. \frac{\partial S}{\partial x_i} \right|_T = 0 \quad (1.35)$$

**2. Vanishing of thermal expansivities** As  $T \rightarrow 0$ , we must have

$$\alpha_J = \left. \frac{1}{x} \frac{\partial x}{\partial T} \right|_J = \left. \frac{1}{x} \frac{\partial S}{\partial J} \right|_T. \quad (1.36)$$

That second equality follows straightforwardly from a Maxwell relation, [which we will go through in the next section...](#)

**3. Vanishing of heat capacities** As  $T \rightarrow 0$ , we can write

$$S(\mathbf{X}, T) - S(\mathbf{X}, 0) = \int_0^T \frac{C_{\mathbf{x}}(T')}{T'} dT', \quad (1.37)$$

but that integral diverges unless

$$\lim_{T \rightarrow 0} C_{\mathbf{x}}(T) \rightarrow 0. \quad (1.38)$$

**Unattainability of absolute zero in a finite number of steps** Loosely, suppose we are cooling a system by systematically reducing some conjugate force (e.g., cooling a gas by adiabatic reductions in pressure). The 3rd Law says that the functions  $S(T)$  for different pressures must all merge at  $T = 0$ , so each step to lower  $T$  must involve progressively smaller changes.

### 1.6.3 Brief discussion

Note that the “vanishing heat capacity” consequence above was (basically) Nernst’s original formulation of the 3rd law! Much disagreement ensued, and the third law’s validity and proper framing was debated hotly contested. Why? Because the 3rd law is very different in character from the other laws of thermodynamics!

**Microscopic origin of the laws** We framed the last few lectures as “Thermodynamics is a phenomenological theory: treat various substances as black boxes and try to deduce a mathematical framework from observations.” But *we know what’s inside the black box (classical mechanics, quantum mechanics)!*

1. 1st law: Conservation of energy (and heat is a form of energy)
2. 0th and 2nd laws: “irreversible approach to equilibrium.” Doesn’t immediately seem to have an analog in microscopic equations of motions, but we’ll try to derive it later as a consequence of  $N \gg 1$ .
3. 3rd law: We’ll soon see statistical mechanical expressions like  $S = k \ln g$ , where  $g$  is a measure of the degeneracy of states:  $S \rightarrow 0 \Rightarrow g = \mathcal{O}(1)$  as  $T \rightarrow 0$ . In classical mechanics, this is simply not true! Just think of an ideal gas!. But, as  $T \rightarrow 0$ , CM is not appropriate. It is hardly surprising, then, that a law whose validity actually rests on quantum mechanics was not well-understood or properly justified before QM itself was.

## 1.7 Various thermodynamic potentials (Appendix H of Pathria)

Mechanical equilibrium occurs at a minimum of a potential energy e.g., the mechanical equilibrium of a mass between springs, etc. etc.. Thermal equilibrium similarly occurs at the extremum of an appropriately defined thermodynamic potential. For example, in our discussion of Clausius’ Theorem (Sec. 1.5.2) we found that the entropy of an adiabatically isolated system increases after any change until it reaches a maximum in equilibrium. But what about systems that are not adiabatically isolated? Or systems which are subject to mechanical work? In this section we will define a handful of thermodynamic potentials that are applicable.

**Analogy with a mechanical system** Briefly, suppose we have a mass on a spring connected to a fixed wall, and let  $x$  be the deviation of the mass’s position away from the equilibrium rest length of the spring. We take the potential energy to be  $U(x) = kx^2/2$ , which is clearly minimized when  $x = 0$ . What if we apply an external force – what will be the new position of the mass? We could define a net potential energy which encompasses this external work,  $H = kx^2/2 - Jx$ , and set the variation of this with respect to  $x$  to be zero:

$$\frac{\partial H}{\partial x} = 0 \Rightarrow x_{eq} = J/k, \quad \text{and} \quad H_{eq} = \frac{-J^2}{2K}. \quad (1.39)$$

### 1.7.1 Enthalpy

What if the system is still adiabatically isolated ( $dQ = 0$ ), but comes to equilibrium under a constant external force? We define *enthalpy*, by analogy with the mechanical example above, as

$$H = E - \mathbf{J} \cdot \mathbf{x}. \quad (1.40)$$

Variations in this quantity are given by

$$dH = dE - d(\mathbf{J} \cdot \mathbf{x}) = TdS + \mathbf{J} \cdot d\mathbf{x} - \mathbf{x} \cdot d\mathbf{J} - \mathbf{J} \cdot d\mathbf{x} = TdS - \mathbf{x} \cdot d\mathbf{J}. \quad (1.41)$$

Note that in general, at constant  $\mathbf{J}$  the work added to the system is  $dW \leq \mathbf{J} \cdot \delta \mathbf{x}$  (where equality occurs for reversible processes), so by the first law and making use of  $dQ = 0$  we have  $dE \leq \mathbf{J} \cdot d\mathbf{x}$ , which means that  $\delta H \leq 0$  as a system approaches equilibrium.

### 1.7.2 Helmholtz Free energy

What if the system is undergoing an isothermal (constant  $T$ ) transformation in the absence of mechanical work ( $dW = 0$ )? We define the Helmholtz free energy

$$F = E - TS, \quad (1.42)$$

which has variations given by

$$dF = dE - d(TS) = TdS + \mathbf{J} \cdot d\mathbf{x} - SdT - TdS = -SdT + \mathbf{J} \cdot d\mathbf{x}. \quad (1.43)$$

Note that Clausius' theorem said that at constant  $T$  the heat added to the system is constrained by  $dQ \leq TdS$ , so making use of  $dW = 0$  we have  $dE = dQ \leq TdS$ , so  $\delta F \leq 0$ .

### 1.7.3 Gibbs Free Energy

What if the system is undergoing an isothermal transformation in the presence of mechanical work done at constant external force? We define the Gibbs free energy by

$$G = E - TS - \mathbf{J} \cdot \mathbf{x}, \quad (1.44)$$

which has variations given by

$$dG = dE - d(TS) - d(\mathbf{J} \cdot \mathbf{x}) = \dots = -SdT - \mathbf{x} \cdot d\mathbf{J}. \quad (1.45)$$

Note that in this case, we have both  $dW \leq \mathbf{J} \cdot \delta \mathbf{x}$  and  $dQ \leq TdS$ , so  $\delta G \leq 0$

### 1.7.4 Grand Potential

Traditionally “chemical work” is treated separately from mechanical work... for chemical equilibrium in the case of no mechanical work, we define the Grand potential by

$$\mathcal{G} = E - TS - \boldsymbol{\mu} \cdot \mathbf{N}, \quad (1.46)$$

where  $\mathbf{N}$  refer to the number of particles of different chemical species, and  $\mu$  refers to the chemical potential for each of them. Variations in  $\mathcal{G}$  satisfy

$$d\mathcal{G} = -SdT + \mathbf{J} \cdot d\mathbf{x} - \mathbf{N} \cdot d\boldsymbol{\mu}. \quad (1.47)$$

## 1.7.5 Changing variables

In the last several subsections we've seen how to use Legendre transformations to move between different natural variables depending on the physical situation we find ourselves in. So, for instance, for adiabatically isolated systems with constant external force, we look at the enthalpy, which has natural variables  $H(\mathbf{J}, S)$ ; for isothermal transformations with no external work we look at the Helmholtz free energy, which has natural variables  $F(\mathbf{x}, T)$ , etc. The equilibrium conjugate variables can then be found by partial differentiation. For instance, the equilibrium force and entropy can be found from  $F$  by

$$J_i = \left. \frac{\partial F}{\partial x_i} \right|_{T, x_{j \neq i}} \quad \text{and} \quad S = - \left. \frac{\partial F}{\partial T} \right|_{\mathbf{x}}. \quad (1.48)$$

Are there any limits on the manipulations we can perform here? For each set of conjugate force/displacement variables, can we always transform to choose whatever we want? *No..* Let's see why

## 1.8 Two bits of math!

### 1.8.1 Extensivity (and Gibbs-Duhem)

Let's look at the differential for  $E$ , including chemical work:

$$dE = TdS + \mathbf{J} \cdot d\mathbf{x} + \mu \cdot d\mathbf{N}. \quad (1.49)$$

*In general* the extensive quantities are proportional to the size of the system, which we can write mathematically as

$$E(\lambda S, \lambda \mathbf{x}, \lambda \mathbf{N}) = \lambda E(S, \mathbf{x}, \mathbf{N}). \quad (1.50)$$

Please note that this is not a requirement, nor does it have the same footing as the rest of the laws of thermodynamics; it is simply a statement about the behavior of "most things."

Let's take the above and differentiate with respect to  $\lambda$  and then evaluate at  $\lambda = 1$ . This gives

$$\left. \frac{\partial E}{\partial S} \right|_{\mathbf{x}, \mathbf{N}} S + \left. \frac{\partial E}{\partial x_i} \right|_{S, x_{j \neq i}, \mathbf{N}} x_i + \left. \frac{\partial E}{\partial N_\alpha} \right|_{S, \mathbf{x}, N_{\beta \neq \alpha}} N_\alpha = E(S, \mathbf{x}, \mathbf{N}). \quad (1.51)$$

Note that the partial derivatives here are (in order)  $T$ ,  $J_i$ , and  $\mu_\alpha$ . This leads to what some people write as the fundamental equation of thermodynamics:

$$E = TS + \mathbf{J} \cdot \mathbf{x} + \mu \cdot \mathbf{N}. \quad (1.52)$$

Combining equations 1.49 and 1.52 lead to a constraint on allowed variations of the intensive coordinates:

$$SdT + \mathbf{x} \cdot d\mathbf{J} + \mathbf{N} \cdot d\mu = 0, \quad (1.53)$$

which is the *Gibbs-Duhem relation*. Again, this is valid for *extensive* systems, as defined by Eq. 1.50. Also, this answers the question at the end of the last section: you cannot (usefully) transform to a potential where the natural coordinates are all intensive, because these intensive coordinates are not all independent.

## 1.8.2 Maxwell relations

“Maxwell relations” follow from combining thermodynamic relationships with the basic properties of partial derivatives. If  $f$ ,  $x$ , and  $y$  are mutually related, we can write

$$df(x, y) = \left. \frac{\partial f}{\partial x} \right|_y dx + \left. \frac{\partial f}{\partial y} \right|_x dy, \quad (1.54)$$

and we will then combine this with symmetry of second derivations,

$$\frac{\partial}{\partial x} \left. \frac{\partial f}{\partial y} \right|_x = \frac{\partial}{\partial y} \left. \frac{\partial f}{\partial x} \right|_y, \quad (1.55)$$

to related various thermodynamic derivatives.

### Example

For instance, let's start with  $dE = TdS + J_i dx_i$ . We know, mathematically, that we can immediately write

$$T = \left. \frac{\partial E}{\partial S} \right|_{\mathbf{x}} \quad \text{and} \quad J_i = \left. \frac{\partial E}{\partial x_i} \right|_{S, x_j \neq i}. \quad (1.56)$$

We can take the mixed derivatives and discover a relationship:

$$\frac{\partial^2 E}{\partial S \partial x_i} = \left. \frac{\partial T}{\partial x_i} \right|_S = \left. \frac{\partial J_i}{\partial S} \right|_{\mathbf{x}}, \quad (1.57)$$

where we might call the latter equality a Maxwell relation.

### Strategy for deriving Maxwell relations

There are several tricks to remembering how to rapidly find the Maxwell relation relevant to a particular expression. In the homework you will go through a method using Jacobian matrices.

Logically, though, it's not so hard to always construct them on the fly. Suppose someone asks you to find a Maxwell relation for

$$\left. \frac{\partial A}{\partial B} \right|_C. \quad (1.58)$$

We'll do the following: (1) write down the fundamental expression for  $dE$ , (2) transform it so that  $A$  will appear in a first derivative and  $B$  and  $C$  are differentials, and (3) profit.

### Worked example:

I want to know  $(\partial\mu/\partial P)|_T$  for an ideal gas.

**Step 1** We write

$$dE = TdS - PdV + \mu dN. \quad (1.59)$$

**Step 2** We note that  $\mu$  is already in a position to appear in first derivatives. Moving on,

$$d(E - PV) = TdS - VdP + \mu dN \quad (1.60)$$

$$d(E - PV - ST) = -TdS - VdP + \mu dN. \quad (1.61)$$

We did not really care what the name of  $(E - PV - ST)$  was, let's just call it  $Y$ . Clearly

$$\mu = \left. \frac{\partial Y}{\partial N} \right|_{T,P} \quad \text{and} \quad V = \left. \frac{\partial Y}{\partial P} \right|_{T,N}, \quad (1.62)$$

so

$$\left. \frac{\partial \mu}{\partial P} \right|_T = \left. \frac{\partial V}{\partial N} \right|_T. \quad (1.63)$$

**Step 3** We're done.