Storyline up to Now

Although you must be familiar with some calculational techniques and representative examples, I believe the general storyline is also important (perhaps more important than various practical topics).

0.0.1 Micro, meso and macro
We live in the macroscopic world of ‘infinitesimal’ time scale about 1 ms and ‘infinitesimal’ length scale about 10 μm. Our cells live in the mesoscopic world where the ‘infinitesimal’ time scale is about 1 ns and ‘infinitesimal’ length scale about 10 pm. The molecules may be described with the ‘infinitesimal’ time scale about 1 fs and ‘infinitesimal’ length scale about 10 am. The adjacent scales are mutually 6 orders apart.

A theoretical framework that tries to describe the world within a single level (in a self-contained fashion) is called a phenomenology. It is distilled from the observations at the relevant level. For example, quantum mechanics is a phenomenology of the microscopic world, and thermodynamics is a phenomenology of a macroscopic world.

0.0.2 Kinetic theory of gases
Daniel Bernoulli’s theory gives

\[ PV = \frac{2}{3} K, \quad (0.0.1) \]

where \( K \) is the average (translational) kinetic energy of one molecule

\[ K = \langle m v^2 / 2 \rangle. \quad (0.0.2) \]

The absolute scale of temperature may be defined as

\[ K = \frac{3}{2} k_B T, \quad (0.0.3) \]

where \( k_B \) is called the Boltzmann constant. Thus,

\[ PV = RT \quad (0.0.4) \]

for one mole of gas particles, where \( R \) is called the gas constant.

0.0.3 Law of large numbers and internal energy
The total kinetic energy \( E \) of an ideal gas is the total (mechanical) energy of the gas. The law of large numbers tells us that

\[ E = NK, \quad (0.0.5) \]

where \( N \) is the total number of particles in the gas. This implies

\[ E = \frac{3}{2} N k_B T \left( = \frac{3}{2} RT, \right. \quad \text{if there are one mole of gas particles}. \quad (0.0.6) \]
0.0.4 Force fluctuation balance in the mesoscopic world gives $k_B$
Einstein pointed out that studying the balance between fluctuation (due to thermal motion) and the external force effect gives $k_B$. For example, the diffusion constant $D$ for a Brownian particle reads

$$D = \frac{k_B T}{\zeta},$$

(0.0.7)

where $\zeta$ is the fluid-particle friction coefficient (say, $6\pi a\eta$, if we use Stokes’ law, $a$ being the radius of the particle, and $\eta$ the shear viscosity). The mean square displacement distance of the particle during time $t$ is given by $\langle R^2 \rangle = 6Dt$. Perrin used this relation to observe $D$.

0.0.5 Avogadro’s constant
$R/k_B$ allows us to observe the number of particles in one mole. This number $N_A$ is called Avogadro’s constant.

0.0.6 Force fluctuation balance gives Boltzmann factor
For a conserved force with potential $U$, the balance between fluctuation and force gives the number density $n(r)$ at position $r$ of (noninteracting) particles in the potential field $U$ as

$$n(r) = n(r')e^{-[U(r)−U(r')]/k_BT}.$$  

(0.0.8)

0.0.7 Thermodynamics is a phenomenology of macroscopic world
We know numerous variables are required to describe the world on the mesoscopic scale, so to make a manageable description of the macroscopic world, we must be ‘highly restrictive’ in choosing the states and the observables we deal with:

1) We handle only equilibrium states that are time-independent, and dissipate no energy.\(^1\)
2) As fundamental concepts we avoid thermal concepts (since we wish to rationalize them by constructing thermodynamics). We choose extensive variables that can be solely described/controlled/observed by macroscopic mechanics and electrodynamics (need not be classical, if macroscopic) as fundamental variables; they are energy and work coordinates. These variables are called thermodynamic coordinates.
3) The space spanned by the thermodynamic coordinates (for a system under study) is called the thermodynamic space.
4) Any equilibrium state has a unique point representing it in the thermodynamic space.\(^2\)
5) A function (or a function of functions) defined on the thermodynamic space is called a state function.

\(^1\)This should be intuitively clear; if the system and the devices that are needed to maintain the system state as a whole require no exchange of energy with the rest of the world for indefinitely long time, the system state is in equilibrium.
\(^2\)Unfortunately, a point in the thermodynamic space can correspond not only to an equilibrium state, but also infinitesimally close states that may be extremely slowly changing irreversibly (e.g., hot coffee in a good thermos), so be careful about the converse.
0.0.8 The First law of thermodynamics

The first law of thermodynamics is essentially the conservation of energy $E$ described in terms of work coordinates.\(^3\) According to the ways to exchange work with the system the total work $W$ given to the system may not be identical to the change of the system internal energy $\Delta E$. The discrepancy is called heat $Q$:

$$\Delta E = W + Q.$$ \hfill (0.0.9)

There is a special condition that makes $\Delta E = W$. This is called the adiabatic condition.\(^4\) Thus, the first law is

(i) $E$ is a state function.
(ii) Its change between two equilibrium states may be the sum of work and heat supplied to the system.

Under adiabatic condition $dE$ may be described by the differentials of the work coordinates as

$$dE = -PdV + BdM + xdX,$$ \hfill (0.0.10)

where $X$ is the (generic) work coordinate and $x$ its conjugate intensive variable; $(x, X)$ is called a conjugate pair. Thus $(V, -P)$ is a conjugate pair (do not forget the negative sign).

0.0.9 The Second law of entropy

If the initial and the final states have identical work coordinates, $\Delta E > 0$ (Planck’s law).

This allows us to foliate the thermodynamic space into isentropic hypersurfaces, each of which cross any of a line with constant work-coordinates at most once. Thus, we may introduce a differentiable monotone increasing function $S$ of energy called entropy; if there is no work coordinate change (which is reversible)

$$dS = dQ/T.$$ \hfill (0.0.11)

If a change is adiabatic and reversible, $dS = 0$; we cannot get out of $S = \text{constant}$ surface; only cooling can decrease $S$ while keeping all the work-coordinates constant; thus any engine needs a radiator.

0.0.10 Quasistatic process

If the initial and the final states are in equilibrium, they are in the thermodynamic space. However, the process that has brought the initial state to the final state may not be in this space, because the intermediate states may not be close to any equilibrium state.

If the change is sufficiently slow, then all the intermediate states may be close to some equilibrium states, so we can draw the process as a path in the thermodynamic space. However, this is not enough for us to use thermodynamics step by step along the path, because still dissipation could occur (as in the case of hot coffee in a good thermos); thermodynamics can be applied only when we can retrace the path backward while erasing all the trace of the forward change from the world. Such a slow process is called a quasistatic process.

We can use the differential form of the thermodynamic relations only along quasistatic

---

\(^3\)For the work coordinates to be well-defined, the change can not be too fast, so the first law is not the most general energy conservation law.

\(^4\)That is, no net heat exchange is the condition. You need not out the system in a Dewar jar.
path in the thermodynamic space. Therefore, to apply thermodynamics to compute the change of state functions quantitatively always we must (i) Identify the initial and the final equilibrium states, (ii) Invent convenient quasi-equilibrium process connecting these processes. (ii) is because the change of state functions do not depend on the actual paths.

0.0.11 Gibbs relation
Infinitesimally,
\[ dE = dQ + dW. \] 
(0.0.12)

If the change is quasistatic, then this reads
\[ dE = TdS - PdV + BdM + xdX, \] 
(0.0.13)
which is called the Gibbs relation.

The entropic version of the Gibbs relation reads
\[ dS = \frac{1}{T}dE + \frac{P}{T}dV - \frac{B}{T}dM - \frac{x}{T}dX. \] 
(0.0.14)

0.0.12 Clausius’ inequality
If a system is thermally isolated, we know
\[ \Delta S \geq 0. \] 
(0.0.15)

If the system is allowed to exchange heat \( Q \) with the external world that stays in equilibrium, then the external world giving \( Q \) to the system loses entropy by \( Q/T_{ex} \), but the surrounding environment + the system is as a whole thermally isolated, so (0.0.15) implies
\[ \Delta S - \frac{Q}{T_{ex}} \geq 0 \] 
(0.0.16)
or Clausius’ inequality
\[ \Delta S \geq \frac{Q}{T_{ex}}. \] 
(0.0.17)

0.0.13 Max entropy principle and concavity of entropy
In a thermally isolated system, entropy cannot decrease. Therefore, if it reaches its maximum value under the condition, the system cannot change under isolation. Thus, if entropy is max in isolation, the system is in equilibrium (max entropy principle).

The extensivity of thermodynamic variables and entropy thus implies that \( S(E, X) \) is a concave function of thermodynamic coordinates.
0.0.14 Isothermal processes
If the initial and the final states of a process is equilibrium states with the same temperature, we say the process is an isothermal process. For this to be realizable, the system must exchange heat freely with its surroundings. Therefore, it is convenient to study $dE - dQ$:

$$dE - TdS = d(E - TS) = dW. \quad (0.0.18)$$

We define the Helmholtz free energy as $A = E - TS$: its Gibbs relation reads

$$dA = -SdT - PdV + BdM + xdX \quad (0.0.19)$$

0.0.15 Minimum free energy principle
If a process is quasistatic, $\Delta A = W$. However, if not reversible, Clausius’ inequality implies

$$\Delta A \leq W; \quad (0.0.20)$$

the work you put into the system is not effectively changed into its energy, because heat generated dissipation of mechanical forces must be discarded.

This means that if all the work coordinates are unchanged, then along a natural process $A$ decreases. Thus, if $A$ is minimum under isothermal condition, the system cannot change. The equilibrium state is reached, if $A$ is minimized under isothermal condition (minimum free energy principle).

0.0.16 Legendre transformation
$A$ is formally defined as $E - TS$, but this $T$ must be chosen to be compatible with the system $E$ and $S$. That is,

$$\left( \frac{\partial E}{\partial S} \right)_x = T. \quad (0.0.21)$$

An elementary geometry gives

$$A = \min_E [E - TS] = \min_S [E - TS]. \quad (0.0.22)$$

This is usually called ther Legendre transformation in thermodynamics, but in mathematics (and much more rationally; see 0.0.17)

$$-A = \max_S [TS - E] \quad (0.0.23)$$

is called the Legendre transformation.

0.0.17 Convexity analysis
Let $f(x)$ be a convex function. Then, its Legendre transformation $f^*$ defined as

$$f^*(y) = \max_x [xy - f(x)] \quad (0.0.24)$$
is again a convex function, and $f^{**} = (f^*)^* = f$:
\[ f(x) = \max_y [xy - f^*(y)]. \tag{0.0.25} \]
That is, Legendre transformation perfectly preserves the functional information.

0.0.18 Massieu function
In thermodynamics $S - E/T = -A/T$ is called the Massieu function. As you will see shortly, entropy is much more fundamental statistically than energy, so $-A/T$ is more natural 'physically' than $A$ itself.

0.0.19 Legendre transformation of $S$
We know $S$ is concave, so $-S$ is a convex function of $E$. Make the following Legendre transformation (note that $T$ is fixed in the following calculation)
\[ (-S)^* = \max_E [(-1/T)E - (-S)] = \max_E [S - E(1/T)] = \frac{1}{T} \max_E [TS - E] = -\frac{A}{T}. \tag{0.0.26} \]
Thus, $A/T$ is a concave function of $-1/T$, but since $-1/T$ is a monotone function of $T$, $A$ itself is concave as a function of $T$. This implies $E$ is a convex function of $S$ and work coordinates.

0.0.20 Statistical mechanics
Although thermodynamics is powerful, it cannot give us any materials scientific concrete information that should be sensitive to microscopic details. Thus, we need a tool that can connect two different scale levels, say, micro and macro. Thus statistical mechanics was conceived.

Basically what we need is a micro-macro translation table. The thermodynamic coordinates are defined in terms of mechanics, so their microscopic expressions are straightforward. Thus, the only nontrivial element is $S$. This was guessed by Boltzmann as Boltzmann’s principle:
\[ S = k_B \log W(E, X), \tag{0.0.27} \]
where $W(E, X)$ the number of microstates compatible with the thermodynamic state $(E, X)$. $W$ is called the microcanonical partition function, and the set of all the microstates compatible with $(E, X)$ is called the microcanonical ensemble.

Following Einstein, we know this principle can be thermodynamically justified.

0.0.21 Isothermal system
For an isothermal system it is convenient to use $A$ (or $-A/T$), so we wish to have a microscopic translation of this quantity.

Our starting point is the Legendre transformation
\[ -\frac{A}{T} = \max_E [(-1/T)E - (-S)]. \tag{0.0.28} \]
From this we get

\[ e^{-\beta A} = \max_E e^{S-E} = \max_E W(E)e^{-\beta E}. \]  

(0.0.29)

This is already a translation, but we can usually show

\[ e^{-\beta A} = \sum_{E>0} W(E)e^{-\beta E} \equiv Z(T). \]  

(0.0.30)

\[ Z \] is called the canonical partition function, and (0.0.29) and this formula differs only \( O[\log N/N] \). Thus

\[ Z(T) = \sum_{\Gamma} e^{-\beta E} \]  

(0.0.31)

with

\[ A = -k_B T \log Z \]  

(0.0.32)

is called the canonical formalism.\(^5\)

\[ \]  

\[ \textbf{0.0.22 Ensamble equivalence} \]

Thanks to the convex analysis if we can know one thermodynamic potential, we can know the rest completely. The statistical mechanical counterpart is the ensemble equivalence. The key mathematical observation for this to be true is that as long as we ignore the relative error of order \( \log N/N \)

\[ \max_X Z(X)e^{-\beta x X} = \int dX Z(X)e^{-\beta x X}. \]  

(0.0.33)

\[ ^5\text{Actually, Einstein justified this formula thermodynamically directly.} \]