“The proper study of biology should really begin with the theme of energy and its transformations.”
Albert L. Lehninger (from *Bioenergetics: The Molecular Basis of Biological Energy Transformations*)

A. Introduction and Basic Principles

- **Energy:** The capacity to do work.
  
  Energy assumes many forms: potential, kinetic, thermal, electrical, etc. The transformation of energy from one type into another is of central importance in biology. Energy transformation is an important capability of a living cell.

- **Thermodynamics:** The field which describes and quantifies energy transformations.
  
  - Describes the transfer of work and heat from one equilibrium state to another.
  
  - Advantages of Thermodynamics: Very general tool for describing energy transformations. Can be used to describe transformations of energy in very complicated and perhaps not thoroughly defined systems. Thermodynamics describes energy transformations in the *macroscopic* world.
  
  - Disadvantages: The generality of thermodynamics can be disarming. The formalism of thermodynamics is couched in the calculus of functions of several variables. Detailed, *microscopic* information is lost.

  
  - Range of Validity:
  
    - Thermodynamics can describe *average* properties of large amounts of *ordinary* matter. It can describe the energetics of living things (i.e. bioenergetics).
    
    - Thermodynamics does NOT describe how long a process takes to convert a system from one equilibrium state to another.
    
    - Thermodynamics does not describe fluctuations, i.e. brief excursions from equilibrium involving small quantities of matter (e.g. Brownian motion).
    
    - The validity of thermodynamics at cosmological scales is questionable.

**Comment:** To apply thermodynamics to a living system (or any system) one need not have knowledge of the detailed, microscopic structure of the system. One need not even be aware of the existence of atoms or molecules. However the changes in a living system that thermodynamics describes at a macroscopic level, have an underlying reality in mechanics, which describes the positions and motions of individual atoms, molecules, etc. The relationship between the thermodynamic (i.e. macroscopic) view of a system undergoing change, and the mechanical (i.e. microscopic) view of a changing system consisting of a very large number of particles (i.e. atoms, molecules, etc) was explored.
briefly in Ch. 1 of the text and in Lectures 1-3. In Ch. 2 and 3, and in the next 6-7
Lectures, the thermodynamic method for studying complicated systems at the
macroscopic level will be explored.

B. Methodology and Basic Assumptions of Thermodynamics

- It is assumed, for the purpose of solving energy transformation problems, that the
  universe is divided into two parts, the system and the surroundings.
- The system is divided from the surrounding by a boundary. The nature of the
  boundary must be defined carefully. In particular it must be established what may or
  may not pass through the boundary.
- Open system: matter and energy may pass through the boundary between the
  system and the surroundings.
- Closed system: matter may not cross the boundary between the system and the
  surroundings. Energy may be exchanged between the system and the
  surroundings, however.
- Isolated system: Neither energy nor matter may cross the boundary.
- Equilibrium: Consider a complicated system (e.g. a large number of molecules)
  which undergoes a change from an initial state A to a final state B. This may, for
  example, involve a chemical reaction where reactant molecules (i.e. the A state)
  converted to product molecules (the B state).

\[
\begin{align*}
A & \xrightarrow{R_f} B \\
& \xleftarrow{R_r}
\end{align*}
\]

When the rate (R_f) at which reactant molecules are converted to product
molecules equals the rate (R_r) at which product molecules are converted back to reactant
molecules, (i.e. R_f=R_r) a state of equilibrium exists.
- If there is a net conversion of molecules from the A state to the B state (or vice
  versa), such that the A state (or B state) becomes depleted of molecules, net transport
  is said to have occurred. If net transport occurs, a system is not at equilibrium.
- A system at equilibrium is described by a set of state variables, which includes
  pressure (P), temperature (T), volume (V), and composition (described by a set of
  mole amounts \{n_i\}).
- Assume a single component system (e.g. an ideal gas) with molar amount n.
  There are four state variables: P, V, T, n. These variables are related by an
  equation of state. As discussed in Lectures 1-3, the equation of state for an ideal
  gas is \(PV=nRT\). Thus the state variables are not independent quantities. Only three
  of the four state variables are independent, because once three are measured, the
  fourth can be calculated from the equation of state.
- Changes between equilibrium states are quantified by changes in state functions.
- A state function \(F\) is a function of the state variables \(P, V, T, \{n_i\}\).
- A state function is defined when a system reaches equilibrium.
- Thermodynamics provides means to calculate changes in state variables when a
  system passes from an initial equilibrium state to a final equilibrium state. That is, thermodynamics enables us to calculate \(\Delta F = F(\text{final}) - F(\text{initial})\).
Unlike mechanics, thermodynamics does not provide a means to calculate $F$...only $\Delta F$. However, some exceptions exist (see the discussion on the Third Law).

State function changes $\Delta F$ are only dependent on the initial state of the system, described by $P_{\text{initial}}$, $V_{\text{initial}}$, $T_{\text{initial}}$, $n_{\text{initial}}$, and the final state of the system, described by $P_{\text{final}}$, $V_{\text{final}}$, $T_{\text{final}}$, and $n_{\text{final}}$. State function changes do not depend upon the details of the specific path followed (i.e. the trajectory).

Quantities that are path-dependent are not state functions.

Differentials: Thermodynamic state functions are functions of several state variables including $P$, $V$, $T$, and $n$. The state variable $n$ is easily eliminated by considering molar quantities. Of the three remaining state variables only two are independent because of the constraint imposed by the equation of state. A small change in a state function $F$ is $dF$ where $\Delta F = \int_{\text{initial}}^{\text{final}} dF$.

Changes in state functions can be expressed in differential form. For a differential of the state function $E$: $dE = \left(\frac{\partial E}{\partial T}\right)_V dT + \left(\frac{\partial E}{\partial V}\right)_T dV$ which physically means if the temperature or the volume of a material change the energy changes.

A differential $dZ$ has the general form $dZ(x, y) = M(x, y)dx + N(x, y)dy$.

If $\frac{\partial M}{\partial y} = \frac{\partial N}{\partial x}$ the differential is exact (Euler’s Criterion). It follows that exact differentials have the form $dZ = \left(\frac{\partial Z}{\partial x}\right)_y dx + \left(\frac{\partial Z}{\partial y}\right)_x dy$.

All state functions are exact differentials.

The path integrals of exact differentials are invariant to path. From this fact it follows that for a state function $F$ $\Delta F = F_{\text{final}} - F_{\text{initial}} = \int_{\text{initial}}^{\text{final}} dF$.

Proof by Construction: Consider a differential $dZ = 2xy \cdot dx + x^2 dy$ integrated on two paths where Path I is $x=y$ and Path II is $x^2=y$. The integrations are from $(x,y)=(0,0)$ to $(x,y)=(1,1)$.
• Path integral along Path I:

\[
\Delta Z_I = \oint_C dZ = 2 \oint_C xy \cdot dx + \oint_C x^2 dy
\]

\[
= 2 \int_0^1 x^2 dx + \int_0^1 y^2 dy = 1
\]

• Path integral along Path II:

\[
\Delta Z_{II} = \oint_C dZ = 2 \oint_C xy \cdot dx + \oint_C x^2 dy
\]

\[
= 2 \int_0^1 x^3 dx + \int_0^1 y dy = 1
\]

So the integral of an exact differential is independent of path and only dependent on the initial and final states. This is an important property of state functions.

• Contrast this behavior with the inexact differential \( dZ = xy \cdot dx + xy \cdot dy \).

\[
\Delta Z_I = \oint_C dZ = \int_0^1 xy \cdot dx + \int_0^1 x^2 dy
\]

\[
= \int_0^1 x^2 dx + \int_0^1 y^2 dy = \frac{2}{3}
\]

and

\[
\Delta Z_{II} = \oint_C dZ = \int_0^1 xy \cdot dx + \int_0^1 x^2 dy
\]

\[
= \int_0^1 x^3 dx + \int_0^{1/2} y^{3/2} dy = \frac{11}{15}
\]