I. Thermodynamics

I.A Fundamental definitions

• **Thermodynamics** *is a phenomenological description of equilibrium properties of macroscopic systems.*

⋆ As a *phenomenological* description, it is based on a number of empirical observations which are summarized by the laws of thermodynamics. A coherent logical and mathematical structure is then constructed on the basis of these observations, which leads to a variety of useful concepts, and to testable relationships among various quantities. The laws of thermodynamics can only be justified by a more fundamental (microscopic) theory of nature. For example, statistical mechanics attempts to obtain these laws starting from classical or quantum mechanical equations for the evolution of collections of particles.

⋆ A system under study is said to be in *equilibrium* when its properties do not change appreciably with time over the intervals of interest (observation times). The dependence on the observation time makes the concept of equilibrium subjective. For example, window glass is in equilibrium as a solid over many decades, but flows like a fluid over time scales of millennia. At the other extreme, it is perfectly legitimate to consider the equilibrium between matter and radiation in the early universe during the first minutes of the big bang.

⋆ The *macroscopic system* in equilibrium is characterized by a number of *thermodynamic coordinates* or *state functions*. Some common examples of such coordinates are pressure and volume (for a fluid), surface tension and area (for a film), tension and length (for a wire), electric field and polarization (for a dielectric), $\cdots$. A *closed* system is an idealization similar to a point particle in mechanics in that it is assumed to be completely isolated by *adiabatic walls* that don't allow any exchange of heat with the surroundings. By contrast, *diathermic walls* allow heat exchange for an *open* system. In addition to the above mechanical coordinates, the laws of thermodynamics imply the existence of other equilibrium state functions as described in the following sections.

I.B The zeroth law

The zeroth law of thermodynamics describes the transitive nature of thermal equilibrium. It states:

• *If two systems, A and B, are separately in equilibrium with a third system C, then they are also in equilibrium with one another.*

Despite its apparent simplicity, the zeroth law has the consequence of implying the existence of an important state function, the *empirical temperature* Θ, such that systems in equilibrium are at the same temperature.

Proof: Let the equilibrium state of systems A, B, and C be described by the coordinates $\{A_1, A_2, \cdots\}$, $\{B_1, B_2, \cdots\}$, and $\{C_1, C_2, \cdots\}$ respectively. The assumption that A and C are in equilibrium implies a constraint between the coordinates of A and C, i.e. a change in A_1 must be accompanied by some changes in $\{A_2, \cdots; C_1, C_2, \cdots\}$ to maintain equilibrium of A and C. Denote this constraint by

$$f_{AC}(A_1, A_2, \cdots; C_1, C_2, \cdots) = 0. \tag{I.1}$$

The equilibrium of B and C implies a similar constraint

$$f_{BC}(B_1, B_2, \cdots; C_1, C_2, \cdots) = 0. \tag{I.2}$$

Each of the above equations can be solved for C_1 to yield

$$\begin{aligned} C_1 =& F_{AC}(A_1, A_2, \cdots; C_2, \cdots), \\ C_1 =& F_{BC}(B_1, B_2, \cdots; C_2, \cdots). \end{aligned} \tag{I.3}$$

Thus if C is separately in equilibrium with A and B we must have

$$F_{AC}(A_1, A_2, \cdots; C_2, \cdots) = F_{BC}(B_1, B_2, \cdots; C_2, \cdots). \tag{I.4}$$

However, according to the zeroth law there is also equilibrium between A and B, implying the constraint

$$f_{AB}(A_1, A_2, \cdots; B_1, B_2, \cdots) = 0. \tag{I.5}$$

Therefore it must be possible to simplify eq.(I.4) by cancelling the coordinates of C. Hence, the condition (I.5) for equilibrium of A and B must be expressible as

$$\Theta_A(A_1, A_2, \cdots) = \Theta_B(B_1, B_2, \cdots), \tag{I.6}$$

i.e., equilibrium is characterized by a function Θ of thermodynamic coordinates. This function specifies the *equation of state*, and *isotherms* of A are described by the condition $\Theta_A(A_1, A_2, \cdots) = \Theta$.

Example: Consider three systems: (A) a wire of length L with tension F, (B) a paramagnet of magnetization M in a magnetic field B, and (C) a gas of volume V at pressure P. Observations indicate that when these systems are in equilibrium, the following constraints are satisfied between their coordinates:

$$\begin{aligned} \left(P + \frac{a}{V^2}\right)(V-b)(L-L_0) - c[F - K(L-L_0)] = 0, \\ \left(P + \frac{a}{V^2}\right)(V-b)M - dB = 0. \end{aligned} \tag{I.7}$$

Clearly these constraints can be organized into three empirical temperature functions as

$$\Theta \propto \left(P + \frac{a}{V^2}\right)(V-b) = c\left(\frac{F}{L-L_0} - K\right) = d\frac{B}{M}. \tag{I.8}$$

These are the well known equations of state describing:

$$\begin{cases} \left(P + a/V^2\right)(V-b) = Nk_BT & \text{(van der Waals gas)} \\ M = (N\mu_B^2 B)/(3k_BT) & \text{(Curie paramagnet)} \\ F = (K+DT)(L-L_0) & \text{(Hook's law for rubber)} \end{cases} . \tag{I.9}$$

The ideal gas temperature scale: As the above example indicates, the zeroth law merely states the presence of isotherms. In order to set up a practical temperature scale at this stage, a reference system is necessary. The *ideal gas* occupies an important place in thermodynamics and provides the necessary reference. Empirical observations indicate that the product of pressure and volume is constant along the isotherms of any gas that is sufficiently dilute. The ideal gas refers to this *dilute* limit of real gases, and the ideal gas temperature is proportional to the product. The constant of proportionality is determined by reference to the temperature of the triple point of the ice–water–gas system, which was set to 273.16 degrees Kelvin (^0K) by the 10^{th} General Conference on Weights and Measures in 1954. Using a dilute gas (i.e. as $P \to 0$) as thermometer, the temperature of a system can be obtained from

$$T(^oK) \equiv 273.16 \times \left(\lim_{P\to 0} (PV)_{\text{system}} / \lim_{P\to 0} (PV)_{\text{ice-water-gas}} \right). \tag{I.10}$$

I.C The First law

We now consider transformations between different equilibrium states. Such transformations can be achieved by applying *work* or *heat* to the system. The first law states that both work and heat are forms of *energy*, and that the total energy is conserved. We shall use the following formulation:

• *The amount of work required to change the state of an otherwise adiabatically isolated system depends only on the initial and final states, and not on the means by which the work is performed, or on the intermediate stages through which the system passes.*

As a consequence, we conclude the existence of another state function, the internal energy, $E(\mathbf{X})$. Up to a constant, $E(\mathbf{X})$ can be obtained from the amount of work ΔW needed for an *adiabatic* transformation from an initial state $\mathbf{X_i}$ to a final state $\mathbf{X_f}$, using

$$\Delta W = E(\mathbf{X_f}) - E(\mathbf{X_i}). \tag{I.11}$$

In a generic (*non–adiabatic*) transformation, the amount of work does not equal to the change in the internal energy. The difference $\Delta Q = \Delta E - \Delta W$ is defined as the heat intake of the system from its surroundings. Clearly in such transformations, ΔQ and ΔW are not separately functions of state, in that they depend on external factors such as the means of applying work, and not only on the final states. To emphasize this, for a differential transformation we write

$$đQ = dE - đW, \tag{I.12}$$

where $dE = \sum_i \partial_i E dX_i$ can be obtained by differentiation, while $đQ$ and $đW$ generally can not. Also note the convention that the signs of work and heat are chosen to indicate the energy *added* to the system, and not vice versa.

A *quasi-static* transformation is one that is performed sufficiently slowly so that the system is always in equilibrium. Thus at any stage of the process, the thermodynamic coordinates of the system exist and can in principle be computed. For such transformations, the work done on the system (equal in magnitude but opposite in sign to the work done by the system) can be related to changes in these coordinates. Typically one can divide the state functions $\{\mathbf{X}\}$ into a set of *generalized displacements* $\{\mathbf{x}\}$, and their conjugate *generalized forces* $\{\mathbf{J}\}$, such that for an infinitesimal quasi-static transformation

$$đW = \sum_i J_i dx_i. \tag{I.13}$$

Table [1] provides some common examples of such coordinates. Note that the displacement is usually an *extensive* quantity, i.e. proportional to system size, while the forces are *intensive* and independent of size. Also note that pressure is by convention calculated from the force exerted by the system on the walls, as opposed to the force on a spring which is exerted in the opposite direction. This is the origin of the negative sign that usually accompanies hydrostatic work.

System	Force		Displacement	
Wire	Tension	F	Length	L
Film	Surface Tension	$\mathcal{S}$	Area	A
Fluid	Pressure	$-P$	Volume	V
Magnet	Magnetic Field	H	Magnetization	M
Dielectric	Electric Field	E	Polarization	P
Chemical Reaction	Chemical Potential	μ	Particle Number	N

Table 1: Generalized Forces and Displacements

Joule's Free Expansion Experiment: Another important property of the ideal gas is the behavior of its internal energy. Observations indicate that if such a gas expands adiabatically (but not necessarily quasi-statically), from a volume V_i to V_f, the initial and final temperatures are the same. Since the transformation is adiabatic ($\Delta Q = 0$) and there is no external work done on the system ($\Delta W = 0$), the internal energy of the gas is unchanged. Since the pressure and volume of the gas change in the process, but its temperature does not, we conclude that the internal energy depends only on temperature, i.e. $E(V,T) = E(T)$. This property of the ideal gas is in fact a consequence of the form of its equation of state as will be proved in problem set [2].

Response functions are the usual method for characterizing the macroscopic behavior of a system. They are experimentally measured from the changes of thermodynamic coordinates with external probes. Some common response functions are:
Heat Capacities are obtained from the change in temperature upon addition of heat to the system. Since heat is not a function of state, the path by which it is supplied must also be specified. For example, for a gas we can calculate the heat capacities at constant volume or pressure, denoted by $C_V = đQ/dT|_V$ and $C_P = đQ/dT|_P$ respectively. The latter is larger since some of the heat is used up in the work done in changes of volume:

$$\begin{aligned} C_V &= \left.\frac{đQ}{dT}\right|_V = \left.\frac{dE - đW}{dT}\right|_V = \left.\frac{dE + PdV}{dT}\right|_V = \left.\frac{\partial E}{\partial T}\right|_V , \\ C_P &= \left.\frac{đQ}{dT}\right|_P = \left.\frac{dE - đW}{dT}\right|_P = \left.\frac{dE + PdV}{dT}\right|_P = \left.\frac{\partial E}{\partial T}\right|_P + P \left.\frac{\partial V}{\partial T}\right|_P . \end{aligned} \tag{I.14}$$

Force Constants measure the (infinitesimal) ratio of displacement to force and are generalizations of the spring constant. Examples include the isothermal compressibility of a gas $\kappa_T = -\partial V/\partial P|_T /V$, and the susceptibility of a magnet $\chi_T = \partial M/\partial B|_T /V$. From the equation of state of an ideal gas $PV \propto T$, we obtain $\kappa_T = 1/P$.
Thermal Responses probe the change in the thermodynamic coordinates with temperature. For example, the expansivity of a gas is given by $\alpha_P = \partial V/\partial T|_P /V$, which equals $1/T$ for the ideal gas.

Since the internal energy of an ideal gas depends only on its temperature, $\partial E/\partial T|_V = \partial E/\partial T|_P = dE/dT$, and eq.(I.14) simplifies to

$$C_P - C_V = P \left.\frac{\partial V}{\partial T}\right|_P = PV\alpha_P = \frac{PV}{T} \equiv Nk_B. \tag{I.15}$$

The last equality follows from extensivity: for a given amount of ideal gas, the constant PV/T is proportional to N, the number of particles in the gas; the ratio is Boltzmann's constant with a value of $k_B \approx 1.4 \times 10^{-23} J^0 K^{-1}$.