3.1 Introduction to Equilibrium Statistical Mechanics

Basic reference: C. Thompson, Classical Equilibrium Statistical Mechanics, Oxford University Press

3.2 Summary of Thermodynamics:

3.2.1 Zeroth Law of Thermodynamics

A state of equilibrium exists and is transitive, i.e., if A is in equilibrium with B, and B with C, then A is in equilibrium with C.

3.2.2 First Law of Thermodynamics

Corresponding to system A is an internal energy function $U_A$ which depends on the state of the system, such that the work done in going from state $(P_1, V_1)$ to the state $(P_2, V_2)$ in any adiabatic process is

$$
\Delta W = U_A(P_1, V_1) - U_A(P_2, V_2) = -\Delta U_A
$$

independently of the path from state 1 to 2.

The amount of heat $Q_A$ absorbed by system A in any change of state is

$$
Q_A = \Delta U_A + \Delta W
$$

for an infinitesimal change,

$$
\delta Q = dU + PdV
$$
3.2.3 Second Law of Thermodynamics

Let us first define the terms:

An adiabatic curve is a solution of the first-order differential equation

\[
(P + \frac{\partial U}{\partial V})dV + \frac{\partial U}{\partial P}dP = 0
\]

which is derived from the equation \(\delta Q = dU + PdV = 0\) for a quasi-static adiabatic process.

A Carnot cycle is the reversible cyclic process in figure 1.

Using the first law to evaluate the components of the Carnot cycle \(C\) we can check directly that the total work done \(W\) during the cycle is

\[
W = \int_C PdV = Q_1 - Q_2
\]

Define the efficiency of the process to be

\[
e = \frac{W}{Q_1} = 1 - \frac{Q_2}{Q_1}
\]

3.2.4 Kelvin’s Statement of the Second Law

There does not exist any cyclic process for extracting heat from a substance and converting it entirely to work, i.e., there cannot be any perpetual motion machine.

3.2.5 Consequences of the Second Law

(i) The efficiency \(e\) of a Carnot cycle depends only on \(T_1\) and \(T_2\) but not on the particular system in the cycle.

(ii) Fact (i) implies that \(\frac{Q_2}{Q_1} = f(T_1, T_2)\) is a universal function of the temperatures \(T_1\) and \(T_2\).

(iii) The function \(f(T_1, T_2)\) in (ii) must have the form

\[
f(T_1, T_2) = \frac{H(T_1)}{H(T_2)}
\]

in terms of some universal function \(H\). We define \(L = \alpha H(T)\) for some constant scale factor \(\alpha\), to be the absolute temperature.
3.2. SUMMARY OF THERMODYNAMICS:

(iv) Thus, the efficiency $e$ of any Carnot cycle operating at absolute temperatures $\theta_1$ and $\theta_2$ is given by:

$$e = 1 - \frac{\theta_2}{\theta_1}$$

3.2.6 Carnot’s Theorem:

For any closed reversible cycle $C_R$:

$$\oint_{C_R} \frac{\delta Q}{\theta} = 0$$

Therefore,

$$\frac{\delta Q}{\theta} = dS$$

is an exact differential of a function $S = S(V, \theta)$ of the state of the system. We call $S$ the entropy.

3.2.7 Clausius’s Theorem:

For any cycle $C$

$$\oint_{C} \frac{\delta Q}{\theta} \leq 0$$

with equality if the cycle is reversible.

3.2.8 Alternative Statement of the Second Law

(a) For reversible changes, there is an absolute temperature $\theta$ such that $\frac{\delta Q}{\theta}$ is an exact differential of a function $S$ known as the entropy.

(b) For irreversible changes in a thermally isolated system, the entropy never decreases.
3.3 Thermodynamics and Statistical Mechanics

The Helmholtz free energy is defined to be:

$$\Psi = U - \theta S$$

where $\theta$ is the absolute temperature.

The Gibbs free energy is defined to be

$$F = U - \theta S + PV$$

or

$$F = U - \theta S - HM$$

where $H$ is the magnetic field and $M$ the magnetization.

3.3.1 Essential Properties:

$\Psi$ never *increases* for isolated systems at constant temperature $\theta$.

$F$ never *increases* for a system at constant pressure and temperature.

Remark. The equilibrium states for a system correspond to states of minimum $\Psi$ and $F$.

By assuming that $\Psi$ and $F$ are functions of any two of the three variables $P, V, T$ we obtain important thermodynamic relations such as:

Take $\Psi = \Psi(V, \theta)$. Then $\Psi = U - \theta S$ implies:

\[
\begin{align*}
    d\Psi &= dU - \theta dS - S d\theta \\
    &= \delta Q - P dV - \theta dS - S d\theta \\
    &= -P dV - S d\theta
\end{align*}
\]

after using the first and second laws of thermodynamics. Then:

\[
\begin{align*}
    P &= -\left(\frac{\partial \Psi}{\partial V}\right)_\theta \\
    S &= -\left(\frac{\partial \Psi}{\partial \theta}\right)_V
\end{align*}
\]
which implies that one of Maxwell’s relations is true:

$$\left( \frac{\partial P}{\partial \theta} \right)_V = \left( \frac{\partial S}{\partial V} \right)_\theta$$ \hspace{1cm} (3.3)

For magnetic systems we have the corresponding expressions:

$$H = \left( \frac{\partial \Psi}{\partial M(\theta)} \right)_T$$ \hspace{1cm} (3.4)

$$S = -\left( \frac{\partial \Psi}{\partial \theta} \right)_M$$ \hspace{1cm} (3.5)

Using the Gibbs free energy \( F \), we obtain

$$M = -\left( \frac{\partial F}{\partial H} \right)_T$$ \hspace{1cm} (3.6)

$$S = -\left( \frac{\partial F}{\partial \theta} \right)_H$$ \hspace{1cm} (3.7)

From these we can obtain in turn the isothermal compressibility defined by

$$\kappa_T^{-1} = -V \left( \frac{\partial P}{\partial V} \right)_\theta$$

$$= V \left( \frac{\partial^2 \Psi}{\partial V^2} \right)_\theta$$

and the isothermal susceptibility defined by

$$\chi_T = \left( \frac{\partial M}{\partial H} \right)_\theta = -\left( \frac{\partial^2 F}{\partial H^2} \right)_T$$

Specific heats are given by

$$C_V = -\theta \left( \frac{\partial^2 \Psi}{\partial \theta^2} \right)_V$$

$$C_H = -\theta \left( \frac{\partial^2 F}{\partial \theta^2} \right)_H$$
In general, we have

\[ C_x = \left( \frac{\delta Q}{\theta} \right)_x = \theta \left( \frac{\partial S}{\partial \theta} \right)_x \]

### 3.3.2 Consequences of Physical Constraints:

**(A)** The isothermal compressibility \( \kappa_T \geq 0 \) on physical grounds which implies that

\[ \left( \frac{\partial^2 \Psi}{\partial V^2} \right)_\theta \geq 0 \]

i.e., \( \Psi \) is convex.

**(B)** The pressure \( P \geq 0 \) implies that \( \Psi \) is a *monotonic non-increasing* function of \( V \).

Combining facts (A) and (B), we arrive at the conclusion that \( \Psi(V, \theta) \) is a convex monotonically decreasing function of \( V \) for fixed \( \theta \).

Non-negative isothermal susceptibility, i.e.,

\( \chi_T \geq 0 \)

implies that

\[ \left( \frac{\partial^2 F}{\partial H^2} \right)_T \leq 0 \]

or \( F \) is a concave function of \( H \).

### 3.4 Conclusion.

We end Lecture 3 on classical thermodynamics on the note that the ultimate goal of classical equilibrium statistical mechanics is to provide physically correct forms for the Helmholtz Free Energy \( \Psi \) and the Gibbs Free Energy \( F \) on the basis of a microscopic theory.

While this theory is a molecular theory in most cases, there are now sufficient examples of good applications of statistical mechanics where this theory is nonmolecular.