Lecture 6

Pathria Ch. 1, L.L. Ch. 11

Thermodynamics - is a phenomenological theory of matter. It is directly related to experiment.

Fundamental concepts of thermodynamics

1) A thermodynamic system is any macroscopic system.

2) Thermodynamic quantities are measurable macroscopic quantities associated with a system such as:

<table>
<thead>
<tr>
<th></th>
<th>Intensive</th>
<th>Extensive</th>
</tr>
</thead>
<tbody>
<tr>
<td>P - pressure</td>
<td>T</td>
<td>S</td>
</tr>
<tr>
<td>V - volume</td>
<td>P</td>
<td>E</td>
</tr>
<tr>
<td>T - temperature</td>
<td>H</td>
<td>V</td>
</tr>
<tr>
<td>H - magnetic field</td>
<td>E</td>
<td>W</td>
</tr>
</tbody>
</table>

3) Thermodynamic quantities are related to each other. These relations are called thermodynamic relations.

4) A thermodynamic state is specified by a set of values of thermodynamic quantities necessary for description of the system.

5) Thermodynamic equilibrium is the thermodynamic state when it does not change with time.
The state variables determine uniquely the equilibrium state, independent of the way this state was reached.

Starting from state $A$, the state variable $Z$ of the state $B$ can be obtained by

$$Z(B) = Z(A) + \int_{0_1}^{0_2} dZ$$

From this follows, that for

$$y = \gamma_1 - \gamma_2$$

closed path,

$$\oint dZ = 0$$

This is equivalent to the statement that $Z$ is an exact differential, i.e. it is single-valued in the space of states.

$$dZ = \left( \frac{\partial Z}{\partial X} \right)_Y dX + \left( \frac{\partial Z}{\partial Y} \right)_X dY$$

As we will see later, not every measurable quantity is an exact differential. Examples of such quantities are the different forms of work and heat.
Example 1

Let us consider two systems in thermal equilibrium forming a closed system.

<table>
<thead>
<tr>
<th>$T_1$</th>
<th>$T_2$</th>
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After some time, equilibrium will be established between the bodies and finally $T_1' = T_2'$.

$t_2 > t_1$  

During the process, the total entropy $S = S_1 + S_2$ must increase

\[
\frac{dS}{dt} > 0
\]

Since the total energy is conserved

\[
\frac{dE}{dt} = \frac{dE_1}{dt} + \frac{dE_2}{dt} = 0 \implies \frac{dE_2}{dt} = -\frac{dE_1}{dt}
\]

\[
\frac{dS}{dt} = \frac{dS_1}{dE_1} \frac{dE_1}{dt} + \frac{dS_2}{dE_2} \frac{dE_2}{dt} = \left(\frac{dS}{dE_1} - \frac{dS}{dE_2}\right) \frac{dE_1}{dt} = \left(\frac{1}{T_1} - \frac{1}{T_2}\right) \frac{dE_1}{dt} > 0
\]

$t_2 > t_1$ \implies $\frac{dE_1}{dt} > 0$ and $\frac{dE_2}{dt} < 0$

With time the energy of the second system decreases, while the energy of the first body increases.

Energy passes from the hot to the cold system.
Units of temperature:

\[ T \rightarrow [K] \quad \text{Kelvin} \]

\[ k_B T \rightarrow [J] \quad \text{Joule, or eV} \]

\[ k_B = 1.38 \times 10^{-23} \text{ J/K} = 8.6 \times 10^{-5} \frac{\text{eV}}{K} \]

We will also use

\[ \beta = \frac{1}{k_B T} \quad \text{- inverse temperature} \]

Adiabatic process

1. System is thermally isolated
2. External fields change so slowly that the entropy \( S \) practically does not change

What does this mean mathematically?

Let us describe an external field by \( A \).

\[ \frac{dS}{dt} = f \left( \frac{dA}{dt} \right) \]

Since \( \frac{dA}{dt} \) is small, we can expand

\[ \frac{ds}{dt} \]

in powers of \( \frac{dA}{dt} \). We note that \( f(0) = 0 \).

\[ \Rightarrow \frac{ds}{dt} = f \left( \frac{dA}{dt} \right) = k_1 \frac{dA}{dt} + k_2 \left( \frac{dA}{dt} \right)^2 + \ldots \]
\( \frac{dS}{dt} \) can be either positive or negative, but \( \frac{dS}{dt} > 0 \), and therefore, \( k_1 = 0 \).

\[
\frac{dS}{dt} = k_2 \left( \frac{dA}{dt} \right)^2
\]

\[
\frac{dS}{dA} \frac{dA}{dt} = k_2 \left( \frac{dA}{dt} \right)^2 \Rightarrow \frac{dS}{dA} = k_2 \frac{dA}{dt}
\]

If \( \frac{dA}{dt} \to 0 \), then \( \frac{dS}{dA} \to 0 \), which proves that

adiabatic process is reversible.

In accordance with the law of increase of the entropy, the reversible process can take place only when the entropy of the closed system remains constant. If the entropy increases, the reverse process cannot take place and the process is called irreversible.

Pressure

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Pathridt Chapter 1

First we note that if the body is in thermal equilibrium, then the entropy of the body depends only on the volume of the body but not on its shape.

\[ V \rightarrow V \] * The change of the volume of the system necessarily changes entropy, as it is an additive quantity.
the change of the shape of the body can be regarded as a rearrangement of its individual parts so that neither the energy nor the entropy of the body changes.

\[ S = S(E, V) \]

Let us assume gas in a chamber and compute the force \( \mathbf{F} \) exerted by gas on the surface bounding its volume.

- radius vector of the element of the surface.

\[ \mathbf{F} = -\frac{\partial \mathbf{E}(p, q, \mathbf{r})}{\partial \mathbf{r}} \]

the force acting on the surface element \( d\mathbf{s} \).

If the volume changes, then \( \mathbf{F} = \mathbf{F}(t) \).

Let us consider adiabatic process: \( S = \text{const} \)

\[ \langle \mathbf{F} \rangle = -\left( \frac{\partial \mathbf{E} (p, q, \mathbf{F})}{\partial \mathbf{F}} \right) = - \left( \frac{\partial \mathbf{E}}{\partial \mathbf{r}} \right)_S = - \left( \frac{\partial \mathbf{E}}{\partial V} \right)_S \frac{\partial V}{\partial \mathbf{r}} = - \left( \frac{\partial \mathbf{E}}{\partial V} \right)_S \mathbf{p} d\mathbf{s} \]

the surface element

\[ d\mathbf{s} = \hat{n} ds \]
We obtained that the mean force on a surface element is normal to the surface element and proportional to its area.

\[ \mathbf{F} = - \left( \frac{\partial E}{\partial V} \right)_S \mathbf{N} \]

The magnitude of the force per area is called pressure:

\[ P = - \left( \frac{\partial E}{\partial V} \right)_S \]

Let us consider here how the temperature has been introduced:

\[ T = \frac{\partial E}{\partial S} \]

If the volume changes, then the full differential of energy should be written as

\[ dE = Tds - PdV \]