Thermal Physics Notes

Shashwat Chakraborty (200260049)

$U_i(n_i, P_i, V_i, \ldots)$

$W = -nRT \int_{V_i}^{V_f} \frac{dV}{V} = -nRT \ln\left(\frac{V_f}{V_i}\right)$ $H = U + PV$ $T(K) = T(°C) + 273.15$

$U_f(n_f, P_f, V_f, \ldots)$ $C_p = (\Delta H / \Delta T)_P$ $dH = dU + d(PV)$ $dH = dU + pdV + Vdp$

$dU = dq + dw$ $C_p = \left(\frac{\partial H}{\partial T}\right)_p$ $\Delta U = Q - W$

$dH = dq - pdV + Vdp$ $W = P\Delta U$ $\Delta S = nRT \ln\left(\frac{V_f}{V_i}\right)$

$H = U + PV$ $dH = C_p dT$ $W = \int_{V_1}^{V_2} PdV$

$dw = -pdV$ $\Delta S = \frac{\Delta_{trs} H}{T}$ $\Delta H = q_p = C_p \times \Delta T$ $C_v = (\Delta U / \Delta T)_V$

$C_v = \left(\frac{\partial U}{\partial T}\right)_v$ $dS \geq \frac{dq}{T}$

$\Delta U = m(u_2 - u_1) \Delta KE$
$= \frac{1}{2}m(v_2^2 - v_1^2) \Delta PE$
$= mg(z_2 - z_1)$

$dS = \frac{dq_{rev}}{T}$

$\Delta S = \int_i^f \frac{dq_{rev}}{T}$

$W_b = \frac{P_2 V_2 - P_1 V_1}{1-n}$ $\eta_{th} = \frac{W_{net}}{Q_{in}} = 1 - \frac{Q_{out}}{Q_{in}}$ $Q = \Delta U + P\Delta V$

$dH = dq + Vdp$ / $\Delta H = \Delta U + V\Delta p$

$dH = (dq)_p$ / $\Delta H = q_p$ $T_R = \frac{T}{T_{cr}}$ $dU = C_v dT$ $x = \frac{m_g}{m_f + m_g}$

$dU = (dq)_v$ / $\Delta U = q_v$ $\Delta U = q_v = C_v \times \Delta T$ $V_R = \frac{V P_{cr}}{RT_{cr}}$

$P_R = \frac{P}{P_{cr}}$ $W_b = P_1 V_1 \ln \frac{V_2}{V_1}$ $= RT_1 \ln \frac{P_1}{P_2}$ $\Delta U = U_f - U_i = q \text{ (heat)} + w \text{ (work)}$

$= P_1 V_1 \ln \frac{P_1}{P_2}$

Contents

1 | Lecture 1

Reference book: Herbert B. Callen - Thermodynamics and Thermostatistics
- `https://drive.google.com/file/d/11ygKClITZgF4yU05_UyhQ4CKt7QYX9wQ/`
`view?usp=sharing`
Let's get started!

- Laws of thermodynamics apply to macroscopic objects/collections of particles $\rightarrow$ systems with many interactions

- For Newton's Laws, you need the positions, velocities and the model/type of inter-particle forces present in order to predict the evolution of the system.

- Macroscopic systems $\rightarrow$ General Laws $\rightarrow$ Universal in nature (applicable to a wide variety of systems)

- These laws are not fundamental $\rightarrow$ Emerge from microscopic laws $\rightarrow$ But they make the analysis of macroscopic properties simple

- Example: Consider a box with N ideal gas particles $\rightarrow$ We need 6N coordinates, i.e., 3-spatial coordinates and 3-velocity components for each particle $\rightarrow$ Law: $\vec{F}_i = m_i \vec{a}_i$ (3 second-order differential equations).

  Let's try to find what *coordinates* describe macroscopic systems $\rightarrow$ Thermodynamic variable

  Consider a 1-D lattice (say a metal rod) with separation between adjacent particles $= a$. The particles are held together so they are vibrating about their mean position. Plot the displacement of ith particle Δx_i against i. As N (total number of particle) is very large we can look ath the scenario wherein $N \rightarrow \infty$, i.e., the particle number-axis becomes

approximately continuous. We will see "collective behaviour" because there motions are connected. At a later time, the curve shifts forward $\rightarrow$ analogy: wave that is propagating forward.

$k = \frac{2\pi}{\lambda}$

$\omega(k)$: dispersion relation

Modes:

1. Slow mode:
   (a) Small k modes
   (b) Large λ modes
   (c) Small ω modes

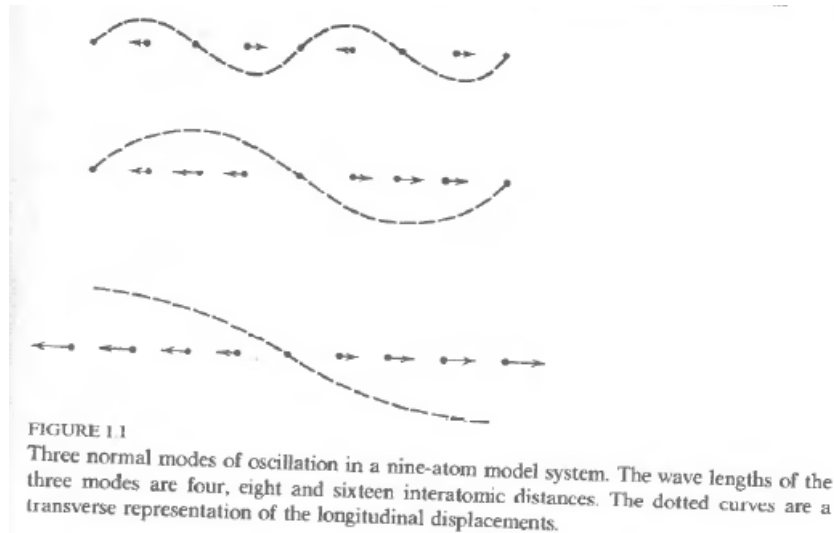   "Long distance modes" $\rightarrow \lambda >> a$

2. Fast mode:
   (a) Large k modes
   (b) Small λ modes
   (c) Large ω modes - oscillate rapidly

   "Short distance modes" $\rightarrow \lambda \approx a$

\# When we observe time average, the high frequency modes are un-observable $\rightarrow$ "Things that don't change over long time interval are macroscopic observables". Take the limits $\lambda \rightarrow \infty$ and $T \rightarrow \infty$, the states that emerge are called "Thermodynamic States"/ "Static States".

\# When we take into account the extremely large wavelength modes, we see that particles on one side move in a certain direction (say left) and particles on the other side move in the opposite direction (right). Overall effect: Length of the rod appears to be increasing $\rightarrow$ Macroscopic effect $\rightarrow$ Length of rod: macroscopic variable $\rightarrow$ Volume of solid: thermodynamic coordinate

FIGURE 1.1
Three normal modes of oscillation in a nine-atom model system. The wave lengths of the three modes are four, eight and sixteen interatomic distances. The dotted curves are a transverse representation of the longitudinal displacements.

- Some examples of macroscopic variables:

    1. Electrostatics: Macroscopic variable $\rightarrow$ Net charge (Q)

    2. Magnetostatics: Macroscopic value $\rightarrow$ net magnetic dipole moment ($\vec{\mu}$)

- Speciality of thermodynamics $\rightarrow$ Takes into account "hidden coordinates". Tells us energy is distributed among the modes which are invisible to us at a macroscopic level!

2 | Lecture 2

- Idealizations and Simplifications:

    1. Electrical: Uncharged/unpolarized

    2. Mechanical: Inelastic/in-compressible

- "Simple systems" → On a macroscopic level: Homogeneous and isotropic and surface effects are negligible. Not acted upon by electric/magnetic/gravitational fields.

- For simple systems

    1. No macroscopic electrical coordinate (net dipole moment or quadrupole moment etc.)

    2. No elastic shear and other such mechanical parameters

    3. Volume (V) remains a relevant mechanical parameter! → macroscopic compression or extension is possible → Volume is, therefore, a thermodynamic variable that can be changed by macroscopic forces.

    4. Chemical composition: Number of moles (n) → $n = \frac{\text{Number of atoms/molecules of species}}{\text{Avogadro's number } (N_A)}$

    > **Macroscopic definition of a mole:** A sample weighing 12 grams of ^{12}C contains 1 mole of ^{12}C. Thus, 12g is assigned to be the molar mass of ^{12}C. Molar masses of other isotopes stand in the same ratio as the "atomic masses".

Atomic Masses (g) of Some Naturally Occurring Elements (Mixtures of Isotopes)[a]

H	1.0080	F	18.9984
Li	6.941	Na	22.9898
C	12.011	Al	26.9815
N	14.0067	S	32.06
O	15.9994	Cl	35.453

[a] As adopted by the International Union of Pure and Applied Chemistry, 1969.

5. Mole fraction: In a mixture of k species the mole-fraction χ i^{th} species is:

$$\chi_i = \frac{N_i}{\sum_{r=1}^{k} N_r}$$

6. Molar volume: It is given by the ratio of the total volume of mixture and the total number of moles.

$$\text{Molar Volume} = \frac{V}{\sum_{r=1}^{k} N_r}$$

- Example: Consider 2 mixtures named A and B. Thermodynamics variables of A $\rightarrow (V^A, N_1^A, N_2^A, N_3^A, ...)$ and those of B $\rightarrow (V^B, N_1^B, N_2^B, N_3^B, ...)$. Now, consider a mixture C=A+B, its thermodynamic variables will be $(V^A + V^B, N_1^A + N_1^B, N_2^A + N_2^B, N_3^A + N_3^B, ...)$. Conclusion: The thermodynamic variables we discussed above are additive! # Additive thermodynamic coordinates are called **extensive**.

- Internal Energy: It is an extensive parameter. At a microscopic level, the energy is the simply $\frac{1}{2}mv^2 + U$ which is a conserved quantity, although at the macroscopic level it is not obvious!

> **Noether's Theorem:** In Layman's terms, if a system with conservative forces has continuous symmetry property, then there are corresponding conserved quantity.

- Macroscopic systems have *definite* and *precise* energy. In order to think of energy as thermodynamic variable, we need to know about its "measurability" and "controllability". Also, we are not interested in absolute energy instead we are interested in the change in energy (ΔE).

- Thermodynamic internal energy: $u = E - E_0$, where E_0 is the energy of fiducial state/reference energy level. u is an extensive parameter.

- "Heat is a form of energy transfer!"

- Thermodynamic equilibrium: In general, systems subside to very simple states after long time. These very "simple" states don't depend on the previously applied external influences. These terminal simple states are called "equilibrium states".

> **Postulate 1:** There exist particular terminal states (equilibrium states) of simple systems that, at a macroscopic level, are characterized *completely* by $(u, V, N_1, N_2, ...)$.
>
> \# Of course, for more general systems, there can be more parameters.

- Meta-stable equilibrium: The equilibrium switches between two states $S1$ and $S2$ either, slowly or very slowly (even macroscopically the transition takes long time to occur).

- Walls/constraints/boundary conditions: Walls of the container are such that the thermodynamic state of the system is fixed. But some of the thermodynamic variables (or all of them) can be changed by relaxing some of the boundary conditions! eg: A container with piston $\rightarrow$ Volume can be changed; A container with semi-permeable wall(s) $\rightarrow$ Number of moles of certain number of species can be changed etc.

   \# Once the system is sealed again, a new equilibrium is eventually attained with new values of the system parameters.