Polymers and biopolymers are large molecules comprising a very large number of monomers (repeating units) in their structure. For any application, the monomers need to be dispersed in a solvent in such a way that the resultant phase is in thermodynamic equilibrium. To understand the phenomena, we need to rely heavily on thermodynamics and statistical concepts. Thus, it is imperative to revisit some of these aspects before discussing the physics of macromolecules.

1.1 Irreversible thermodynamics

The first law of thermodynamics relates the internal energy of a system $U$ with the total heat energy $Q$ and the mechanical work energy $W$ as

$$dU = dQ - dW$$

(1.1)

This has been written in a differential form, meaning that the variation in internal energy is equal to the variation of total heat energy minus that of the mechanical work energy. Based on the first law of thermodynamics, it is possible to categorize any physical system into one of the following:

(i) Isolated system: No mass or heat is exchanged with the surrounding

(ii) Closed system: Only heat is exchanged with the surrounding

(iii) Open system: Both mass and heat are exchanged with the surrounding
Classical thermodynamics suffers from fundamental limitations since this law can only be applied to systems close to equilibrium like reversible processes, and not to open systems, which are commonly encountered in everyday life. We get maximum work out of a reversible process. With irreversible processes, on the other hand, a portion of the energy is spent in the act, for example, as heat – it is unusable energy. This energy is the starting point for the analysis of irreversible thermodynamics. The dissipated energy $\Phi$ per unit time at temperature $T$ is

$$\Phi = T\sigma$$  \hspace{1cm} (1.2)

where $\sigma$ is the local increase in entropy of the system due to the irreversible work. Recall that in a reversible process, the entropy remains the same, whereas in an irreversible process, the unused energy manifests itself by raising the entropy of the system. Therefore, it can be said that entropy is produced in the system wherever irreversible work is done. This conforms with the second law of thermodynamics, which allows entropy either to remain the same (reversible process) or increase (irreversible process). The total entropy change for the system having a volume $V$ will be

$$\int \sigma dV = \frac{dS}{dt}$$  \hspace{1cm} (1.3)

d$S$ is the entropy existing in the system itself. In addition, there is an exchange of entropy with the surrounding, say $d_sS$. The entropy, $S$, like any other thermodynamic function of state or variable, is strictly defined for equilibrium systems. Therefore, the net entropy change, $dS$, that occurs when the system moves from one equilibrium state to another can be described as follows

$$dS = d_sS + d_iS$$  \hspace{1cm} (1.4)

The first part, $d_sS$, arises from the irreversible interaction of the system with the surrounding and is entropy flow from the surrounding. The second part, $d_iS$, is the entropy change which arises from the irreversible changes occurring inside the system – this is the entropy production part given by Eq. (1.3). It is trivial to conclude that

- For isolated systems, $d_sS = 0$,
- For reversible processes, $d_iS = 0$ and
- For irreversible processes, $d_iS > 0$.

As has already been said, this is the result of the second law of thermodynamics. Consequently, the entropy production in any process will be given by

$$dS = dQ/T \text{ (reversible process)}$$

$$dS > dQ/T \text{ (irreversible process)}$$
Combining Eqs (1.1) and (1.5), it can be shown that when the mechanical work is pressure–volume work \(dW = pdV\), for a closed system:

\[
dS = \frac{dU + pdV}{T} \quad \text{(closed system)}
\]

For an open system, this equation can be modified to obtain Gibbs equation:

\[
dS = \frac{dU + pdV}{T} - \sum_i \frac{\mu_i dN_i}{T} \quad \text{(open system)}
\]

Here, \(N_i\) is molar concentration of species \(i\). Gibbs free energy \(G\) and the chemical potential \(\mu_i\) are related by the equation:

\[
\mu_i = \left( \frac{\partial G}{\partial N_i} \right)_{T,P,N_{ij}} \quad \text{(1.8a)}
\]

Differentiating Eq. (1.7) with respect to \(N_i\), gives:

\[
\mu_i = -T \left( \frac{\partial S}{\partial N_i} \right)_{U,V,N_{ij}} \quad \text{(1.8b)}
\]

The first two terms in Gibbs equation [Eq. (1.7)] are the same for a closed system. The last term denotes the entropy change caused by the presence of a solute of species \(i\) with mole fraction \(N_i\) and chemical potential \(\mu_i\). Gibbs equation can also be used to describe the properties of a system over a small length scale such that \(T\), \(P\) and \(\mu_i\) are almost the same at every point but the length scale is large enough to average out all fluctuations. Use of Gibbs equation to describe a system not in equilibrium is one of the postulates in irreversible thermodynamics. It is called the postulate of local equilibrium. Obviously, this cannot be used for systems far away from equilibrium (i.e., shock waves, explosions, etc.).

A detailed analysis of entropy production gives us the following general equation called Euler relation:

\[
\sigma = \sum_{i=1}^{n} \tilde{Y}_i \tilde{X}_i \quad \text{(1.9a)}
\]

which implies that:

\[
dS = \sum_i \dot{X}_i dX_i + \sum Y_i dY_i \quad \text{(1.9b)}
\]
This is the generalized Gibbs–Duhem equation. It reflects the homogeneity of the equilibrium system. We shall provide a detailed and explicit expression for this equation later in this chapter. The Gibbs–Duhem equation shows that there is coupling between flux \( Y_i \) and general thermodynamic force \( X_i \). This can be used as the starting point to study the transport phenomenon in various systems. We also need the following postulates for two reasons: (i) to simplify the mathematics involved and (ii) to discuss transport properties in conjunction with the real physical phenomena occurring in nature.

### 1.2 Postulates in irreversible thermodynamics

1. For a system away from equilibrium, there exists a thermodynamic function for every single part of the system; these functions have values that they would have had, had there been equilibrium.

2. Fluxes \( Y_i \) can be written as linear homogeneous functions of phenomenological forces \( \bar{X}_j \) as

\[
Y_i = \sum_j L_{ij} \bar{X}_j \tag{1.10}
\]

where \( L_{ij} \) are the transport coefficients. These fluxes and forces are the same that we discussed in connection with entropy production.

3. Onsager’s reciprocal relation: \( L_{ij} = L_{ji} \).

### 1.3 Phenomenological forces and fluxes

Within the postulate described above, the equations are given as

\[
Y_1 = L_{11} X_1 + L_{12} X_2 + L_{13} X_3 + \ldots + L_{1n} X_n
\]

\[
Y_2 = L_{21} X_1 + L_{22} X_2 + L_{23} X_3 + \ldots + L_{2n} X_n
\]

Likewise,

\[
Y_n = L_{n1} X_1 + L_{n2} X_2 + L_{n3} X_3 + \ldots + L_{nn} X_n \tag{1.12}
\]

The transport coefficients \( L_{ij} \) are the actual coupling coefficients between the fluxes and the corresponding forces. The principal coefficients \( L_{ii} \) are normally larger than \( L_{ij} \) and \( L_{ii} \gg 0; L_{ii} L_{ij} \gg L_{ij}^2 \).
Let us describe a set of equations containing three forces \( (X_1, X_2, X_3) \) in the following matrix form.

\[
\begin{bmatrix}
  Y_1 \\
  Y_2 \\
  Y_3 \\
\end{bmatrix} =
\begin{bmatrix}
  L_{11} & L_{12} & L_{13} \\
  L_{21} & L_{22} & L_{23} \\
  L_{31} & L_{32} & L_{33} \\
\end{bmatrix}
\begin{bmatrix}
  X_1 \\
  X_2 \\
  X_3 \\
\end{bmatrix}
\]  

(1.13)

This matrix with the coefficients \( L_{ij} \) will be symmetric if \( L_{ij} = L_{ji} \). For a symmetric matrix, it is always possible to define new fluxes \( Y^* \) that are linear combinations of old fluxes \( Y \) and likewise new forces \( X^* \), which are linear combinations of old forces \( X \). At the same time, we can diagonalize the matrix containing the phenomenological coefficients and write

\[
\begin{bmatrix}
  Y_1^* \\
  Y_2^* \\
  Y_3^* \\
\end{bmatrix} =
\begin{bmatrix}
  L'_{11} & 0 & 0 \\
  0 & L'_{22} & 0 \\
  0 & 0 & L'_{33} \\
\end{bmatrix}
\begin{bmatrix}
  X_1^* \\
  X_2^* \\
  X_3^* \\
\end{bmatrix}
\]  

(1.14)

In this way, we have reduced the problem into a much simpler form where the equations are not coupled, giving

\[
Y_1' = L'_{11}X_1'; \quad Y_2' = L'_{22}X_2' \quad \text{and} \quad Y_3' = L'_{33}X_3'.
\]  

(1.15)

We shall use these concepts while discussing transport properties of polymers in their dispersion state.

### 1.4 Gibbs–Duhem equation

Consider a homogeneous dispersion of internal energy \( U \) and volume \( V \) having various solute species \( N_i \) present in the system. Let us assume that there are \( m \) number of solute species present \((0 \leq i \leq m)\). We can define various thermodynamic parameters in the following manner. The entropy of the system \( S \) is given as a function of state variables, that is, \( S = (U, V, N_1, N_2, ..., N_m) \). The system is an open system where mass and energy can be exchanged with the surrounding. At the same time, the population \( N_i \) can also change due to formation of aggregates or decomposition of the species. Thus,

\[
dS = \left( \frac{\partial S}{\partial U} \right)_{V, N} dU + \left( \frac{\partial S}{\partial V} \right)_{U, N} dV + \sum_{i=1}^{m} \left( \frac{\partial S}{\partial N_i} \right)_{U, V, N_{\text{other}}} dN_i.
\]  

(1.16)
If we set \( dN_i = 0 \), Eq. (1.16) will reduce to

\[
dS = \left( \frac{\partial S}{\partial U} \right)_{V,N} dU + \left( \frac{\partial S}{\partial V} \right)_{U,N} dV
\]  

(1.17)

The first law of thermodynamics states that \( dQ = TdS = dU + PdV \), which, on comparison with Eq. (1.17), gives

\[
\left( \frac{\partial S}{\partial U} \right)_{V,N} = \frac{1}{T} \text{ and } \left( \frac{\partial S}{\partial U} \right)_{U,N} = \frac{P}{T}
\]  

(1.18)

Defining chemical potential, \( \mu_i \) as [see Eq. (1.8b)]

\[
\mu_i = -T \left( \frac{\partial S}{\partial N_i} \right)_{U,V,N_{\text{tr}}}
\]  

(1.19)

Equation (1.16) will reduce to

\[
dS = \frac{dU}{T} + \frac{P}{T} dV - \sum_{i=1}^{m} \frac{\mu_i}{T} dN_i
\]  

(1.20)

Thus,

\[
TdS = dU + PdV - \sum_{i=1}^{m} \mu_i dN_i
\]  

(1.21)

Equation (1.21) is the generalized form of the first law of thermodynamics. The extra term on the right-hand side arises from the presence of solute molecules in dispersion that have various concentrations.

Gibbs free energy is given as \( G = U - TS + PV \). Hence,

\[
dG = dU - TdS - SdT + PdV + VdP
\]  

(1.22)

Substituting Eq. (1.21) in Eq. (1.22), one gets

\[
dG = -SdT + VdP + \sum_{i=1}^{m} \mu_i dN_i
\]  

(1.23)

Equation (1.23) is the generalized description of Gibbs free energy.
The internal energy $U$ of this system is defined as

$$U = (S, V, N_1, \ldots, N_m)$$  \hspace{1cm} (1.24)

Recall that the internal energy is an extensive quantity implying that when $S \to \alpha S$, $V \to \alpha V$, $N_i \to \alpha N_i$ and $U \to \alpha U$,

$$U(\alpha S, \alpha V, \alpha N_1, \ldots, \alpha N_m) = \alpha U(S, V, N_1, \ldots, N_m)$$  \hspace{1cm} (1.25)

Let $\alpha = (1 + r)$ with $r << 1$. Equation (1.25) can be rewritten as

$$U((1 + r) S, (1 + r) V, (1 + r) N_1 \ldots (1 + r) N_m) = (1 + r) U$$  \hspace{1cm} (1.26)

This can be expanded in a Taylor series. Neglecting quadratic and higher order terms in $r$

$$U + \left( \frac{\partial U}{\partial S} \right)_{V,N} rS + \left( \frac{\partial U}{\partial V} \right)_{S,N} rV + \sum_{i=1}^{m} \left( \frac{\partial U}{\partial N_i} \right)_{S,V,N_{i\neq j}} rN_i = (1 + r) U$$  \hspace{1cm} (1.27)

This gives

$$U = \left( \frac{\partial U}{\partial S} \right)_{V,N} S + \left( \frac{\partial U}{\partial V} \right)_{S,N} V + \sum_{i=1}^{m} \left( \frac{\partial U}{\partial N_i} \right)_{S,V,N_{i\neq j}} N_i$$  \hspace{1cm} (1.28)

From Maxwell relations, $\left( \frac{\partial U}{\partial S} \right)_{V,N} = T$ and $\left( \frac{\partial U}{\partial V} \right)_{S,N} = -P$

We shall define chemical potential as

$$\mu_i = \left( \frac{\partial U}{\partial N_i} \right)_{S,V,N_{i\neq j}}$$  \hspace{1cm} (1.29)

The definitions of chemical potential given by Eq. (1.19) and Eq. (1.29) are consistent with each other. Now, Eq. (1.28) can be written as

$$U = TS - PV + \sum_i \mu_i N_i$$  \hspace{1cm} (1.30)
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Since, \( G = U - TS + PV \), yet another definition of chemical potential is given by

\[
\mu_i = \left( \frac{\partial G}{\partial N_i} \right)_{P,T,N_{ij}}
\]  \hspace{1cm} (1.31)

This implies that chemical potential is the change in Gibbs free energy per molecule for a given system. Equation (1.30) gives

\[
dU = TdS + SdT - VdP - PdV + \sum_i \mu_i dN_i + \sum_i N_i d\mu_i
\]  \hspace{1cm} (1.32)

Substituting Eq. (1.21) in (1.32), gives

\[
SdT - VdP + \sum_i N_i d\mu_i = 0: \text{Gibbs–Duhem Equation}
\]  \hspace{1cm} (1.33)

We shall be using this equation while discussing transport properties of polymers in their dispersion state.

1.5 Statistical parameters

Let \( u \) be a variable that can assume \( m \) discrete values given by

\[
u_1, \nu_2, \ldots, \nu_m
\]  \hspace{1cm} (1.34)

The probability of occurrence of these events is

\[
P(\nu_1), P(\nu_2), \ldots, P(\nu_m)
\]  \hspace{1cm} (1.35)

Statistical mean is given by

\[
\bar{u} = \langle u \rangle = \frac{P(\nu_1)\nu_1 + P(\nu_2)\nu_2 + \cdots + P(\nu_m)\nu_m}{P(\nu_1) + P(\nu_2) + \cdots + P(\nu_m)}
\]  \hspace{1cm} (1.36)

or

\[
\bar{u} = \sum_{i=1}^m P(\nu_i)\nu_i / \sum_{i=1}^m P(\nu_i)
\]  \hspace{1cm} (1.37)

In most of the cases, the distribution is normalized, meaning

\[
\sum_{i=1}^m P(\nu_i) = 1
\]
If \( u_1, u_2, \ldots, u_m \) are continuous variables, then Eq. (1.37) reduces to

\[
\langle u \rangle = \frac{\int_{u_1}^{u_2} uP(u)du}{\int_{u_1}^{u_2} P(u)du}
\]  

(1.38)

So, if \( f(u) \) is any function of \( u \), its average can be computed as

\[
\bar{f(u)} = \langle f(u) \rangle = \frac{\sum_{i=1}^{m} P(u_i)f(u_i)}{\sum_{i=1}^{m} P(u_i)}
\]  

(1.39)

Similarly, the average of two functions \( f(u) \) and \( g(u) \) are given by

\[
\bar{f(u) + g(u)} = \sum_{i=1}^{m} [f(u_i) + g(u_i)]P(u_i)
\]  

(1.40)

\[
\bar{f(u)} + \bar{g(u)} = \bar{f(u)} + \bar{g(u)}
\]

In the same way, for \( C \) being a constant, the following holds

\[
\bar{Cf(u)} = C\bar{f(u)}
\]  

(1.41)

A more meaningful idea is to compute the standard deviation as

\[
\overline{(\Delta u)^2} = \sum_{i=1}^{m} P(u_i)(u_i - \bar{u})^2 = (u - \bar{u})^2
\]  

(1.42)

This is also called the covariance of the variable.

\[
(u - \bar{u})^2 = u^2 + \bar{u}^2 - 2\bar{u}^2 = \left(\bar{u}^2 - \bar{u}^2\right)
\]  

(1.43)

Hence, from the knowledge of \( P(u) \), one can deduce \( \langle u \rangle, \langle u^2 \rangle, \langle u^3 \rangle, \langle u - \bar{u} \rangle^2, \langle u - \bar{u} \rangle^n \) etc. which provides a complete description of the statistical system.

### 1.6 Probability distributions

In this section, we shall recapitulate the characteristics of some common probability distribution functions and various moments of the variables involved. Any variable that
assumes a range of values can be described through a probability distribution which allows us to define its mean, standard deviation, etc. without ambiguity. Let us look at the properties of some of these functions.

1.6.1 Binomial distribution

It is a very common distribution encountered in everyday life. When a coin is tossed, say \( n \) times, suppose that one obtains head \( x \) times and tail \( (n - x) \) times. The probability of getting a head in this case is \( p \) and a tail is \( q \). Obviously, \( p + q = 1 \). Thus, the probability distribution function that describes the occurrence of \( x \) heads will be given by

\[
P(x) = C_x^n p^x q^{n-x}
\]  

where \( C_x^n = \frac{n!}{x!(n-x)!} \) is called the binomial coefficient.

Realize that Eq. (1.44) is a normalized distribution function, often called Binomial distribution. This is verified as follows

\[
\sum_{x=0}^{n} P(x) = \sum_{x=0}^{n} \frac{n!}{x!(n-x)!} p^x q^{n-x} = (p + q)^n = 1
\]

The above mentioned example implies that the event of tossing a coin is a discrete operation. Thus, the variable assumes only discrete values. Interestingly, Binomial distribution also describes the random walk problem adequately.

The probability distribution given by \( P(x) \) defines the probability of taking \( x \) steps to the right and \( (n - x) \) steps to the left.

The mean is determined by

\[
\overline{x} = \sum_{x=0}^{m} x P(x) = \sum_{x=0}^{n} \frac{n!x}{x!(n-x)!} p^x q^{n-x}
\]  

For any arbitrary \( p \), the following identity holds

\[
\overline{x} = \sum_{x=0}^{n} \frac{n!}{x!(n-x)!} \left[ p \frac{\partial}{\partial p} p^x \right] q^{n-x}
\]  

\[
= n p \frac{\partial}{\partial p} \left[ p^x \right] q^{n-x}
\]

\[
= n p \frac{\partial}{\partial p} \left[ p^x \right] q^{n-x}
\]