CHAPTER 2

THEORY AND EXPERIMENT
2.1 Theory

In the present chapter the theoretical methods for both vibrational dynamics and phase transition are discussed. The chapter is divided into two sections-

- The Wilson’s G.F matrix method modified by Higgs for an infinite polymeric chain is given. The solution to secular equation and their dependence on phase angle gives normal modes and phonon dispersion in the first Brillounin zone (reduced zone scheme). The dispersion curves have been used to obtain density-of-states which in turn gives heat capacity as a function of temperature.

- In the second section the theory of ordered-disordered phase transition is given. The theoretical approach is a variant of Ising model, proposed for ferromagnetism and is utilized by Zimm and Bragg for helix coil transition

2.2 Phonon Dispersion

The theory of phonon dispersion is being discussed under the following heads:-

2.2.1 Molecular Vibrations of Finite Molecules

Common technique applied in vibrational studies is highlighted in this section. We start the discussion for a finite molecule. A molecule consisting of N atoms has 3N-6 vibrational degree of freedoms or 3N-5 vibrational degree of freedoms in case of linear molecule. Mostly Cartesian coordinates are taken into consideration to solve the equation of motion of a vibrating molecule. Apart from Cartesian coordinates, internal coordinates can also be used. In this system position of atoms are described in terms of bond stretches, bond angles and dihedral angles. The benefit of using internal coordinates is that there is less coupling between internal coordinates and also the values of force constants in this picture are easily visualized. Force constants can be relocated from one molecule to other if they belong to the same chemical group.
Wilson’s GF matrix method (1939, 1941, 1955) is one such approach where internal coordinates are used to explain the relative motion between various atoms. To transform the Cartesian coordinates into internal coordinates one writes a matrix as:

\[ R = BX \]  

Eq.(2.1).

Here \( R \) denotes the internal coordinates and \( B \) notates the transformation matrix. The inverse kinetic energy in terms of transformation matrix is given by the relationship:

\[ G_{kl} = \sum_{i=1}^{3n} B_{ki} B_{li} / m_i \]  

Eq.(2.2).

\( k, l=1, \ldots, 3n-6 \)

Where \( m_i \) is mass of \( i^{th} \) atom. Kinetic energy matrix is given by:

\[ 2T = R' G^{-1} R \]  

Eq.(2.3).

Here \( R' \) means transpose matrix of \( R \). To find the potential energy one uses the relationship:

\[ 2V = R' F R \]  

Eq.(2.4).

\( V \) is the potential energy matrix and the elements \( F_{kl} \) are the force constants. The molecular vibrational problem attains the form as shown in the matrix equation below:

\[ GFL = L\lambda \]  

Eq.(2.5).

Equation of vibrational frequencies is given by the relation \( \lambda = 4\pi^2 c^2 v^2 \), also the relationship between internal coordinates \( R \) and normal coordinates \( Q \) is represented by:

\[ R = L Q \]  

Eq.(2.6).

Thus the problem of vibrational dynamics attains a secular equation form:
\[ [GF - \lambda I] = 0 \]  \hspace{1cm} \text{Eq.}(2.7).

The above equation unravel the vibrational frequencies. Solution of the matrix equation given by Eq.(2.5) gives the eigenvectors of \( L \). Normal coordinates \( Q \) are related to the internal ones by the linear transformation given by Eq.(2.6). Amount of coupling amongst the diverse internal coordinates in a given normal mode \( Q_k \) are given by the elements of the eigenvector \( L_k \) belonging to the eigenvector \( \lambda_k \). The potential energy distribution (PED) helps to investigate the assistance made from various motions.

2.2.2 Molecular Vibrations of Polymer Chains

The approach which has been discussed in preceding section is also applicable to polymer chains. As one proceeds in this direction it is realized that the order of the matrices becomes infinite. This is so because the polymer is of infinite length thus to reduce the problem to feasible dimensions, the screw symmetry of the polymer chain is considered. The chemical repeat unit of a polymer is built in a regular manner and is repeated along the chain of polymer. It was Higgs (1953) who pointed out the helical symmetry in polymer chain. He employed the symmetry to modify the Wilson’s GF matrix for polymeric systems. Group theoretical ideas were used to categorize the normal modes and derive selection rules for Raman and Infrared spectra.

His model considered an infinite helical molecule to be made up of indistinguishable units mutually joined together such that each unit is linked to the other through a function \( H (l,f) \). This is an operation of translation through unit distance along the polymer axis followed by a rotation through angle \( f \) about the same axis. Thus from a particular unit of the polymer chain we can attain another unit \( \pm n \) away from it just by operating with \( H^n \) (where \( n \) is any positive or negative integer). The transformation
consists of an infinite group which is isomorphic with the infinite cyclic group $C_\infty$. The representations cannot be further reduced and are one dimensional. These are labeled as $\Gamma(0)$ where $0$ is the phase difference of neighboring units and assumes the values in the range $-\pi < 0 < +\pi$. Analogous expression is:

$$\chi(0,H^n) = \exp(in\theta)$$

Eq.(2.8).

Each and every normal mode of vibration related to a molecule must fit in the above representations. We mean to say that if a particular unit vibrates with an amplitude $A$ then the $n^{th}$ unit further apart must vibrate in the same way and will have an amplitude $A\exp(-in\theta)$. If we have a helical molecule then all the frequencies $\nu_i$ of a single chain provides a band of frequencies $\nu_i(0)$. For each frequency $\nu_i(0)$, there corresponds a frequency $\nu_i(-\theta)$ which is equivalent to $\nu_i(0)$. The frequencies belonging to $\Gamma(0)$ degenerate in pairs except for $\nu_i(0)$ and $\nu_i(\pi)$. The complex normal modes can be combined with each other to form two real modes having amplitudes as $(AC\cos n\theta)$ and $(AS\sin n\theta)$.

Let us again consider the vibrational secular equation for this approach. $R_i^n$ denotes the $i^{th}$ internal displacement coordinate associated with the $n^{th}$ chemical unit. The matrix element $F_{nn'}^{ik}$ gives potential interaction between the $i^{th}$ internal coordinate of the $n^{th}$ unit $G_{nn'}^{ik}$ gives kinetic coupling. Due to the periodicity of polymer chain we have:

$$F_{nn'}^{ik} = F_{ik}^{s}$$

Eq.(2.9).

$$G_{nn'}^{ik} = G_{ik}^{s}$$

Eq.(2.10).

Where $s = (n-n')$. Taking this into consideration the infinite inverse kinetic energy matrix ($G$) can be written in term of internal coordinates ($R$) as:
Here $R^n$ denotes column vector related to internal coordinates of the $n^{th}$ chemical unit. The transpose of $G_A$, $G_B$ etc are denoted by $G_A'$, $G_B'$ etc. Similar pattern is observed in $F$ matrix.

The infinite ordered $G$ and $F$ matrices were reduced into finite order by Higg. He factored the matrices into sets of matrices $G(\delta)$ and $F(\delta)$. The order of $G(\delta)$ and $F(\delta)$ is equivalent to $N$. Here $N$ is the number of internal coordinates in chemical repeat unit. A Fourier transform of internal coordinates is given by:

$$S(\delta) = \sum_{n=-\infty}^{\infty} R^n \exp (in\delta) \quad \text{Eq.(2.11).}$$

Using this transformation $G(\delta)$ and $F(\delta)$ matrices attain the form given below:

$$G_{ik}(\delta) = \sum_{n=-\infty}^{\infty} G_{ik}^n \exp (in\delta) \quad \text{Eq.(2.12).}$$
\[ F_{ik}(\delta) = \sum_{n = -\infty}^{\infty} F_{ik}^n \exp \left(\text{i} n\delta\right) \quad \text{Eq.(2.13).} \]

Hence the infinite ordered secular equation can then be reduced into finite order equations:

\[ [G(\delta)F(\delta) - \lambda(\delta)I] = 0 \quad \text{Eq.(2.14).} \]

Here the vibrational frequencies \( \nu(\delta) \) are represented by the equation \( \lambda(\delta) = 4\pi^2 c^2 \nu^2(\delta) \). The frequencies lie in the range given by \(-\pi < \delta < +\pi\) and are expressed in \(\text{cm}^{-1}\).

### 2.2.3 Symmetry Properties and Selection Rules

Among the vibrational frequencies calculated by Eq.(2.14) only some are optically active. Selection rules in terms of the phase difference \( \delta \) and the angle \( \phi \) for infinite polymers were given for the first time by Higgs. We know that the allowed frequencies in infrared spectrum are the ones which belong to representations \( \Gamma(0) \) and they must be present in the representations \( \Gamma(M) \). Vibrations associated with transition moment parallel to the helix axis and the transition moment perpendicular to the helix axis gives rise to infrared spectrum.

To derive the Raman selection rules we have to take the total molecular electric polarizability into account. It can be easily shown that Raman absorption takes place when the vibrations have phase difference \( \delta = 0, \phi, 2\phi \).

### 2.2.4 Calculations on Actual Polymers

Various calculations related to optically active frequencies have been performed in the last few years. According to the theory of crystal spectra it is believed fundamental frequencies taking part in optical absorption are the featured group frequencies. Krimm et. al. (1956, 1958, 1959) interpreted the infrared spectra of various polymers as
polyethylene, poly-tetrafluorethylene and poly-chloro-trifluorethylene by applying these results to polymer chains. Since then Higgs method has been constantly applied for vibrational spectrum calculations of polymers. Miyazawa et. al. (1961, 1962, 1963) and Tadokoro (1960, 1961) used this method to calculate spectroscopically active fundamentals modes of poly-oxymethylene and polypropylene. Schachtschneider et. al. (1964) gave a similar method to calculate spectroscopically active fundamental modes.

Normal mode vibrational analysis for polymeric chain can be done in terms of internal coordinates also. Method described by Piseri et. al. (1968) has been employed in this study. The method has been modified for computers and widespread calculations are done by it. The potential energy can be written in terms of internal coordinates as:

\[ 2V = \sum_{n,n',i,k} F_{ik}^{nn'} R_i^n R_k^{n'} \]  
Eq.(2.15).

The periodicity of the chain implies:

\[ 2V = \sum_{n,i,k} F_{ik}^{n} R_i^n R_k^n + \sum_{n,s,i,k} (F_{ik}^{n} R_i^n R_k^{n+s} + F_{ki}^{n} R_i^{n} R_k^{n+s}) \]  
Eq.(2.16).

Similarly one can write the kinetic energy of the infinite chain:

\[ 2T = \sum_{n,i,k} G_{ik}^{n} P_i^n P_k^n + \sum_{n,s,i,k} (G_{ik}^{n} P_i^n P_k^{n+s} + G_{ki}^{n} P_i^{n+s} P_k^n) \]  
Eq.(2.17).

Using equations Eq.(2.16) & Eq.(2.17), Hamiltonian’s equation of motion can be written. By this we get an infinite number of second order differential equations in terms of \( R_i^{n+s} \). Their solution leads to a planar wave expressed by the equation:

\[ R_i^{n+s} = A_i \exp [-i(\frac{\lambda}{2}t + s\delta)] \]  
Eq.(2.18).

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Where $\delta$ denote the phase shift between two internal coordinates of adjacent units. We get $3p$ simultaneous homogeneous linear equations on substituting Eq.(2.18) in the differential equations. The solutions are given by:

$$G(\delta) = G^o + \sum_s [G^s \exp(i\delta) + G^s' \exp(i\delta)]$$ \hspace{1cm} \text{Eq.(2.19).}$$

$$F(\delta) = F^o + \sum_s [F^s \exp(i\delta) + F^s' \exp(i\delta)]$$ \hspace{1cm} \text{Eq.(2.20).}$$

Fourier transformation of internal coordinates on Higgs method Eq. (2.12) & Eq.(2.13) can yield Eq.(2.19) & Eq.(2.20). The dispersion curves are calculated by taking $\nu(\delta)$ as a function of $\delta$. This is a periodic function with periodic interval of $2\pi$, i.e. $n(\delta) = n(\delta+2\pi)$ also $\nu(-\delta) = \nu(\delta)$. Due to these reasons the study is limited in the range $0 < \delta < \pi$ which corresponds to half of the first Brillouin zone. The infrared active frequencies correspond to values of $\delta = 0, \phi, 2\phi$.

The $G(\delta)$ and $F(\delta)$ matrices are complex for phase difference $\delta$ having value other than 0 or $\pi$. Complex numbers are difficult to calculate due to this reason different methods have been put forward to convert the complex matrices into real ones. For this similarity transformation are made. A complex matrix $H = M+iN$ can be replaced by the real one (Bhagvantam et. al. 1951, Tobin 1955).

Using the above concept we can write $G(\delta) = G^R(\delta) + iG^I(\delta)$ and $F(\delta) = F^R(\delta) + iF^I(\delta)$, where $G^R(\delta), F^R(\delta)$ are real parts and $G^I(\delta), F^I(\delta)$ are the imaginary parts of $G(\delta)$ and $F(\delta)$. Thus the product $H(\delta) = G(\delta) F(\delta)$ becomes:

$$H(\delta) = \begin{vmatrix} G^R(\delta) & -G^I(\delta) \\ G^I(\delta) & G^R(\delta) \end{vmatrix} \times \begin{vmatrix} F^R(\delta) & -F^I(\delta) \\ -F^I(\delta) & F^R(\delta) \end{vmatrix}$$
\[
H(\delta) = \begin{bmatrix}
H^R(\delta) & -H^I(\delta) \\
H^I(\delta) & H^R(\delta)
\end{bmatrix}
\]

Eq.(2.21).

Where
\[
H^R(\delta) = G^R(\delta) F^R(\delta) - G^I(\delta) F^I(\delta)
\]
\[
H^I(\delta) = G^R(\delta) F^I(\delta) + G^I(\delta) F^R(\delta)
\]

Eq.(2.22).

The dimensions of \(H(\delta)\) are now \(2N \times 2N\). At the end problem of complex number has been avoided. Polarization vectors are important outcomes of normal coordinate calculations. These are the components of Cartesian displacements of the atoms in normal modes. For a given mode \(\nu(\delta)\) the polarization vectors are represented by:
\[
q(\delta) = B^{-1}(\delta) L(\delta)
\]

Eq.(2.23).

Where \(L(\delta)\) is obtained from Eq.(2.15).

2.2.5 The Use of Group Theoretical Ideas

Here we are going to discuss the relevance of group theoretical ideas in interpretation of polymer spectrum. As stated previously the modes of a polymer in which all unit cells vibrate in same phase are the ones which are active in Infrared and Raman spectra (Bodewig, 1959). As the symmetry of a helical polymer can be explained by one dimensional spacegroup hence it is sufficient to study factor group containing a translation subgroup. We take an infinite helical polymer consisting of repeat unit having \(n\) chemical units and \(m\) turns (each chemical repeat unit contains \(p\) atoms). Here rotation is the symmetry operation given by \(2\pi m/n\) about the axis of polymer and is followed by a translation of \(l/n\) of the unit cell length along the axis. The factor group is denoted by \(C_{2\pi m/n}\), this is isomorphic with the point group \(C_n\). The factor group of the polymer can predict the number of normal modes, their symmetry properties and
Infrared and Raman activity. When the factor group is attached with dichroic studies of polymer spectra, a study and explanation of the polymer spectra can be done even if the complete normal vibration calculations are not present. Liang et. al. (1956, 1958, 1959) had applied these group theoretical ideas to interpret the spectra of a large number of high polymers such as polyethylene, polytetrafluorethylene, polystrene, polyvinyl chloride, etc. The work was further revised by Krimm (1960).

2.2.6 Force Constants Evaluation

The technique to evaluate force constants is by least square fitting method. To obtain the best fit frequencies, force constants are transferred from the polypeptides having similar conformation. One considers an approximate F matrix called as F₀ and the observed frequencies λₐ₀ to solve the matrix equation:

\[ GF₀L₀ = L₀λ₀ \]  
Eq.(2.24).

Assume \( Δλₐ = λₐ₀ - λₐ₀ \) in above mentioned equation. In the first order approximation we get:

\[ Δλ = J ΔF \]  
Eq.(2.25).

Here J can be calculated from L₀. Corrections of F₀ are calculated so as errors in \( Δλ \) are minimized by using the least square method. So one gets:

\[ J' P Δλ = (J P J) ΔF \]  
Eq.(2.26).

P is a weighing matrix and J’ denotes transposition of J. Solution to the above equation is got by inverting \( JP = J \) to give:

\[ ΔF = (J P J)^{-1} J' P Δλ \]  
Eq.(2.27).

In the case when the number of frequencies is greater than number of matrix elements F, the matrix J’PJ comes out to be nonsingular and corrections ΔF are obtained.
which minimizes the sum of squares of residuals. When corrections are very large breakdown of relation between force constant and frequency term in the Eq.(2.24) occurs. In such cases Taylor expansion of the series involving Δλ_i is needed. Such methodology has been given by King et. al. (1957).

2.2.7 Density-of-States and Heat Capacity

Using dispersion curves the microscopic behavior of the system can be correlated with its macroscopic properties. The frequency distribution function states how energy is dispersed among the different branches of normal modes in the crystal. It is calculated by the relationship given below:

\[ g(\nu) = \sum_j \left( \frac{\partial \nu_j}{\partial \delta} \right)^{-1} |_{\nu_j(\delta) = \nu} \quad \text{Eq.(2.28).} \]

With \[ \int g(\nu_j) \, d\nu_j = 1 \]

The sum is obtained over all the branches j. If a solid is considered as an assembly of harmonic oscillators then the frequency distribution \( g(\nu) \) is its partition function. The partition function can be used to calculate the thermodynamic parameters such as free energy, entropy, enthalpy and specific heat. The Debye relation is used to calculate heat capacity. It can predict important information about the system. As an example it can give information about the proportion of a protein which is in alpha-helical and \( \beta \) sheet structure and is necessary in evaluating the basic thermodynamics of enzyme reaction (Benzinger, 1971).

Debye relation is written below-

\[ C_v = \nu_j g(\nu_j)kN_A(h\nu_j / kT)^2 \frac{\exp (h\nu_j / kT)}{[\exp (h\nu_j / kT) - 1]^2} \quad \text{Eq.(2.29).} \]
We can calculate constant pressure heat capacity $C_p$ by applying Nernst-Lindemann approximation given by (Pan et. al. 1989).

$$C_p - C_v = 3R A_o \left(C_p^2 T/C_v T_{m o}^o\right)$$  \hspace{1cm} \text{Eq.(2.30).}

Where $A_o$ is a constant of a universal value [3.9x10^{-9} (Kmol/J)] and $T_{m o}^o$ is the equilibrium melting temperature (Roles et. al. 1993).

2.3 Phase Transition

Zimm et. al. (1959) modified the Ising model (Ising, 1925) which was initially designed to explain ferromagnetism in one dimensional spin system. Initially Landau et. al. (1938) pointed out that phase transition cannot occur in one dimensional polymeric system but experiments contradicted this theory. The difference in the two is due to the assumptions made in theoretical approach which are as follows:

a) The interaction has a finite range.

b) The interaction is of finite strength.

As soon these assumptions are discarded the phase transition is observed in one dimension. First assumption is removed by taking into consideration the hydrogen bonding between base pairs and nonbounded interactions. Whereas the second one is removed by considering nucleation parameter ($\sigma$). This parameter measures the difficulty in transition from one state to another by introducing singularity in interaction of near about interactions. Thus now phase transition is possible from one state to another. Underneath we discuss the relevant features of the order-disordered transitions, lambda point anomaly and specific heats associated.

2.3.1 Order-Disorder Transitions

The Zimm and Bragg (1959) theory which was initially formed to explain phase transition in one dimension has been modified in three dimensions. The incorporation of
three dimensions and different interactions involved are contained in heat transitions.

The transition matrix presumes the form given below:

\[
P = \begin{pmatrix}
    h & R \\
    1 & \sigma s \\
    1 & s
\end{pmatrix}
\]  

Eq.(2.31).

Here \( \sigma \) is nucleation parameter and \( s \) is growth parameter, \( h \) stands for triple helical state and \( R \) stands for random coil state. The terminology has been considered as taken by Zimm and Bragg. Further calculations lead to the matrix \( T \) and its inverse \( T^{-1} \):

\[
T = \begin{pmatrix}
    1 & 1 \\
    1/(\lambda_1-s) & 1/(\lambda_2-s)
\end{pmatrix}
\]  

Eq.(2.32).

\[
T^{-1} = \begin{pmatrix}
    C_1 & C_1(\lambda_1-1) \\
    C_2 & C_2(\lambda_2-1)
\end{pmatrix}
\]  

Eq.(2.33).

Here \( \lambda_1 \) and \( \lambda_2 \) are the eigen values of matrix \( P \) and are represented as:

\[
\lambda_1 = [(1+s) + \{(1-s) + 4\sigma s\}^{1/2}]/2
\]  

Eq.(2.34).

\[
\lambda_2 = [(1+s) - \{(1-s) + 4\sigma s\}^{1/2}]/2
\]  

Eq.(2.35).

and \( C_1 = \frac{\lambda_4-s}{\lambda_1-\lambda_2} \), \( C_2 = \frac{\lambda_2-s}{\lambda_2-\lambda_1} \)  

Eq.(2.36).

The growth parameter \( s \) is calculated at particular temperature \( T \) and is by the given by equation:

\[
s = \exp \left[ \Delta H(1/T - 1/T_m)/R \right]
\]  

Eq.(2.37).
Here $T_m$ is the transition temperature of the system.

The partition function $Z$ is dependent on the initial state so after assuming that the first unit exist in the helical state we can calculate the partition function which is represented as a row vector having the form given below:

$$U = [0 \ \ \sigma s]$$

The final state can be considered as helical or random with the constraint that both states are equal probable, this can be shown by a column matrix as:

$$V = \begin{bmatrix} 1 \\ 1 \end{bmatrix}$$

The grand partition function $Z$ associated with a macromolecule having $N$ segments can be written as:

$$Z = U P^{N-1} V = U T^{N-1} P^{N-1} T V$$

$$= [0 \ \ \sigma s] \begin{bmatrix} 1 \\ 1 \end{bmatrix} = a_1 \lambda_1^N - a_2 \lambda_2^N$$

Eq.(2.38).

The coefficients $a_1$ and $a_2$ assume the values given by:

$$a_1 = \frac{\sigma s}{\lambda_1 - \lambda_2}, \quad a_2 = \frac{\sigma s}{\lambda_2 - \lambda_1}$$

Eq.(2.39).

Fraction of segments in helical state are denoted by:

$$Q = \frac{\partial (\ln Z)}{N \partial (\ln s)}$$

$$= \frac{s(1-B) \left| \frac{\partial a_1}{\partial s} \right| + s \left| \frac{\partial \lambda_1}{\partial s} \right| - B s \left| \frac{\partial \lambda_2}{\partial s} \right|}{(1-B)}$$
On differentiating Eq.(2.36) and Eq.(2.39), with respect to $s$ we get-

$$\left. \frac{s}{\lambda_1} \frac{\partial \lambda_2}{\partial s} \right| = C_2 \quad \left. \frac{s}{\lambda_2} \frac{\partial \lambda_2}{\partial s} \right| = C_1$$

And also

$$\frac{\partial a_1}{\partial s} = \frac{a_1}{s} - \frac{a_1}{(\lambda_1 - \lambda_2)} \left| \frac{\partial \lambda_1}{\partial s} - \frac{\partial \lambda_2}{\partial s} \right|$$

$$Q = \frac{1 - C_1(1 + B)}{(1 + B)} + \frac{(1 - s - 2s\sigma)}{N(\lambda_1 - \lambda_2)^2}$$

For nondegenerate roots at $N \to \infty$ we get

$$Q = \frac{1 - C_1(1 + B)}{(1 + B)}$$

Substituting $T = T_m$ Eq.(2.37) the value of $s$ comes out to be unity. As $N \to \infty$, the value of $Q$ will be 0.5 at transition temperature. Molar change in enthalpy about transition point is denoted by $\Delta H$.

Vont Hoff enthalpy related to the transition is calculated from the sharpness of the transition at the half width of transition $\Delta T_{1/2}$ (Privalov, 1979).

$$H_{eff} = 4RT_m^2/\Delta T_{1/2}$$

Eq.(2.40).

The number of residues in a joint block melting at a structural unit is calculated from the comparison calculated and experimental enthalpy (Schwarz, 1968).

$$L_0 = \frac{H_{eff}}{H_{exp}}$$

Eq.(2.41).

Relation between nucleation parameter and cooperative length $L_0$ (Schwarz, 1968) is given by:

$$\sigma = 1/ L_0^2$$

Eq.(2.42).
### 2.3.2 Heat Capacity Calculations

After calculating the partition function one can easily find the heat capacity of the molecular chain. Relation between molecular entropy and specific heat changes while undergoing transition from state I to state II is straightforward. The free energy $F$ is given by:

$$ F = -kT \ln Z \quad \text{Eq. (2.43)} $$

In terms of free energy the internal energy $U$ is given by:

$$ U = -T^2 \left. \frac{\partial}{\partial T} \right|_V F $$

The heat capacity can be calculated by the following equation:

$$ C_V = \left. \frac{\partial U}{\partial T} \right|_V = Nk \left| \frac{\Delta H}{RT} \right| \left| s \frac{\partial Q}{\partial s} \right| $$

Where

$$ \frac{\partial Q}{\partial s} = \frac{s(\lambda_1 + \lambda_2)(1 + B)}{(\lambda_1 - \lambda_2)^3(1 - B)} + \left| \frac{\partial B}{\partial s} \right| \frac{(1 - 2C_1)}{(1 - B)^2} + \frac{(2\sigma s - 1)}{N(\lambda_1 - \lambda_2)^2} $$

$$ - \frac{2(1 - s - 2\sigma s)(\lambda_1^2 + \lambda_2^2 - \lambda_1 - \lambda_2)}{Ns(\lambda_1 - \lambda_2)^4} $$

And

$$ \frac{\partial B}{\partial s} = \frac{NB(1 - s)}{s(\lambda_1 - \lambda_2)} $$