

Heat capacity and phonons in poly(L-leucine)

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Abstract. Poly(L-leucine) is one of the polyamino acids having a bulky hydrophobic side-chain. For want of full phonon dispersion curves and density-of-states on this biopolymer Roles *et al* have interpreted their specific heat data in a limited way. In the present communication we report an analysis of the normal modes and their dispersion for poly(L-leucine) which leads to a very good agreement of the specific heat calculations with experimental measurements. It is observed that the main contribution to specific heat comes from the coupling of the back-bone skeletal and side-chain modes. Several other assignments have been revised. A special feature of some dispersion curves is their tendency to bunch in the neighbourhood of helix angle. It has been attributed to the presence of strong intramolecular interactions. Repulsion between the dispersion curves is also observed.

Keywords. Conformation; phonon dispersion; α -helix; normal modes; poly(L-leucine); density-of-states; specific heat.

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1. Introduction

In recent publication Wunderlich and Bu [1], Bu *et al* [2], Roles and Wunderlich [3] and Roles *et al* [4] have reported experimental and theoretical studies of heat capacities of a variety of polymeric systems, synthetic as well as biopolymeric. In most of the cases, their analysis is based on separation of the vibrational spectrum into group and skeletal vibrations. The former are taken from computations fitted to IR and Raman data and the latter by using the two parameter Tarasov model [1] and fitting to low temperature heat capacities. However in a few cases, where detailed dispersion curves of the vibrational spectrum are available [5–9], they have been used for obtaining group and skeletal vibrations and number of vibrators of each type. In some cases, dispersion curves for one polymeric system have been used to obtain the number of vibrators and frequencies of box oscillators for polymers with identical back-bone. This approach is OK when full dispersion curves are not available. However it has its own limitations, specially when the side-chain and back-bone modes are strongly coupled. In the present communication, we report for poly(L-leucine) (PLL), full dispersion curves, density-of-states and specific heat data which is found to be in good agreement with the experimental measurements. Vibrational spectroscopy is an important tool for probing conformation and conformationally sensitive modes of a polymer. In general, the infrared absorption, Raman spectra and inelastic neutron scattering from polymeric systems are very complex and cannot be unravelled without the full knowledge of

dispersion curves. One cannot appreciate without it the origin of both symmetry dependent and symmetry independent spectral features. Further the presence of regions of high density of states which appear in all these techniques and play an important role in thermodynamical behaviour are also dependent on the profile of the dispersion curves. The lack of this information in many polymeric systems has been responsible for incomplete understanding of polymeric spectra. The advent of lasers and fast computers has eased these problems to a large extent. Dispersion curves also provide information on the extent of coupling along the chain together with an understanding of the dependence of the frequency of a given mode upon the sequence length of the ordered conformation. Thus the study of phonon dispersion in polymeric systems continues to be an important one. This group has earlier reported vibrational analyses and phonon dispersion for a variety of biopolymeric systems having α , β , ω , and 3_{10} helical conformation [5–15]. As a part of this continuing programme, we report here a study of normal modes of vibrations and their dispersions for PLL.

Poly(L-leucine) (figure 1) belongs to the class of polyamino acids having bulky hydrophobic side-chains. In solid state, PLL adopts an α -helical conformation and molecular models demonstrate that the formation of α -helix reduces the side-chain to

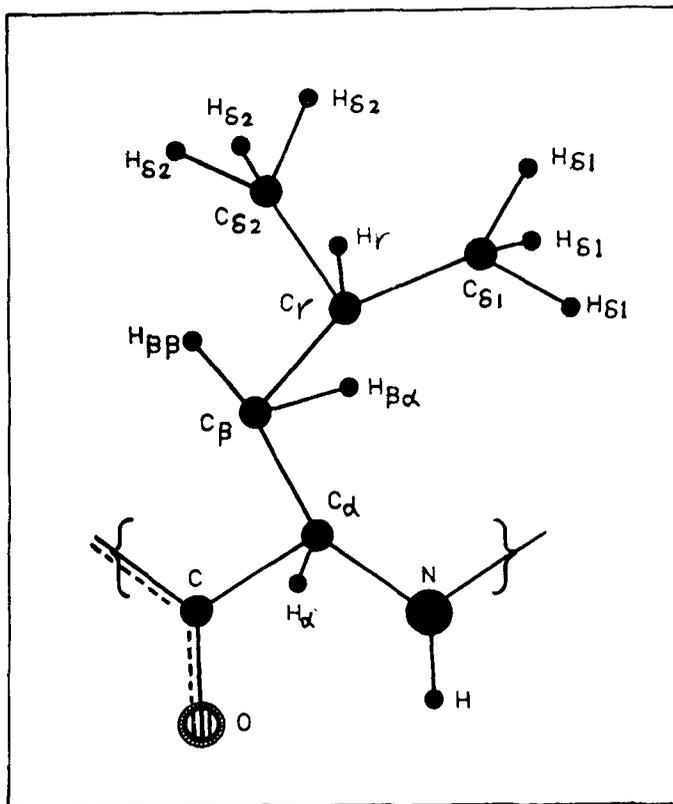


Figure 1. Chemical repeat unit of poly(L-leucine).

side-chain steric interference [16]. Infrared and Raman spectroscopic studies of PLL have been reported by Koenig and Sutton [17] and Itoh *et al* [18]. Their assignments are both incomplete and are based on qualitative considerations. It is, therefore, all the more important to carry out a complete normal mode analysis and their dispersion for PLL. It is through the dispersion curves that one can correlate microscopic behaviour of a crystal with its macroscopic properties such as specific heat.

2. Theory and experiment

2.1 Normal mode analysis

The calculation of normal mode frequencies has been carried out according to Wilson's G F matrix method [19] as modified by Higgs [20] for an infinite chain. The Wilson GF matrix method consists of writing the inverse kinetic energy matrix G and the potential energy matrix F in internal coordinates R . In the case of infinite isolated helical polymer, there are an infinite number of internal coordinates which lead to G and F matrices of infinite order. Due to the screw symmetry of the polymer a transformation similar to that given by Born and Von Karman can be performed which reduces the infinite problem to finite dimensions. The transformation consists of defining a set of symmetry coordinates.

$$S(\delta) = \sum_{s=-\infty}^{\infty} R^s \exp(is\delta)$$

where δ is the vibrational phase difference between the corresponding modes of the adjacent residue units.

The elements of the $G(\delta)$ and $F(\delta)$ matrices have the form:

$$G_{ik}(\delta) = \sum_{s=-\infty}^{\infty} G_{ik}^s \exp(is\delta)$$

$$F_{ik}(\delta) = \sum_{s=-\infty}^{\infty} F_{ik}^s \exp(is\delta)$$

The vibrational secular equation which gives normal mode frequencies and their dispersion as a function of phase angles has the form:

$$[G(\delta)F(\delta) - \lambda(\delta)I] = 0, \quad 0 \leq \delta \leq \pi$$

The vibrational frequencies $\nu(\delta)$ (in cm^{-1}) are related to eigenvalues $\lambda(\delta)$ by the following relation,

$$\lambda(\delta) = 4\pi^2 c^2 \nu^2(\delta) \quad (1)$$

For any given phase difference δ (other than 0 or π), the $G(\delta)$ and $F(\delta)$ matrices are complex. In order to avoid the difficulties involved in handling complex numbers, methods have been devised to transform the complex matrices into equivalent real matrices by constructing suitable linear combinations of coordinates. One method of transforming a complex matrix to its real matrix equivalent is through a similarity transformation. It can be shown that any complex matrix $H = M + iN$ can be replaced

by the real ones.

$$\begin{vmatrix} M & -N \\ N & M \end{vmatrix}$$

In the present case, we can write $G(\delta) = G^R(\delta) + iG^I(\delta)$ and $F(\delta) = F^R(\delta) + iF^I(\delta)$, where $G^R(\delta)$, $F^R(\delta)$, $G^I(\delta)$, $F^I(\delta)$ are the real and imaginary parts of $G(\delta)$ and $F(\delta)$. The product $H(\delta) = G(\delta)F(\delta)$ becomes

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

where

$$H^R(\delta) = G^R(\delta)F^R(\delta) - G^I(\delta)F^I(\delta)$$

$$H^I(\delta) = G^R(\delta)F^I(\delta) + G^I(\delta)F^R(\delta)$$

The matrix $H(\delta)$ now has dimensions $2N \times 2N$. The eigenvalues, therefore, occur in pairs of equal values. The difficulty of dealing with complex numbers is thus avoided.

2.2 Force constant evaluation

The force constants have been obtained by the least square fitting. In order to obtain the 'best fit' with the observed frequencies the following procedure is adopted. Initially, approximate force constants for back-bone are transferred from α Poly(L-alanine) [6]. Thus starting with the approximate F matrix F_0 and the observed frequencies λ_{obs} (related through a constant), one can solve the secular matrix equation

$$GF_0 L_0 = L_0 \lambda_0 \quad (2)$$

Let $\Delta\lambda_i = \lambda_{i_{obs}} - \lambda_{i_0}$ in the above equation. It can be shown that in the first order approximation

$$\Delta\lambda = J\Delta F$$

where J is computed from L_0 . We wish to compute the corrections to F_0 so that the errors $\Delta\lambda$ are minimized. We use the theory of least squares and calculate

$$J'P\overline{\Delta\lambda} = (J'PJ)\overline{\Delta F}$$

where P is a weighting matrix and J' is the transpose of J . The solution to this equation is obtained by inverting $(J'PJ)$ to give

$$\overline{\Delta F} = (J'PJ)^{-1} J'P\overline{\Delta\lambda}$$

If the number of frequencies is greater than the number of F matrix elements, the matrix $J'PJ$ should be non-singular and we obtain the corrections ΔF which will minimize the sum of the weighted squares of the residuals. If the corrections ΔF are fairly large, the linear relation between force constant and frequency term in the matrix eq. (2) breaks down. In such a situation, further refinement using higher order terms in the Taylor's series expansion of $\Delta\lambda_i$ is needed. This procedure has been developed by King *et al* [21].

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The poly(L-leucine) (Lot No. 81H5557, DP(vis)242, Mw 27,4000) was purchased from the Sigma Chemicals, USA. The FTIR spectra (3000–150 cm⁻¹) were recorded in CSI on Perkin-Elmer-1800 spectrophotometer and are shown in figures 2(a) and 2(b). Before running the spectra the equipment was well purged with dry nitrogen.

2.3 Calculation of heat capacity

One of the important uses of dispersion curves is that the microscopic behaviour of a crystal can be correlated with its macroscopic properties such as heat capacity. For a one dimensional system the density-of-state function or the frequency distribution function, which expresses the way energy is distributed among the various branches of normal modes in the crystal, is calculated from the relation,

$$g(\nu) = \sum_j (\partial \nu_j / \partial \delta)^{-1} \Big|_{\nu_j(\delta) = \nu} \quad (3)$$

The sum is over all branches j . Considering a solid as an assembly of harmonic oscillators, the frequency distribution $g(\nu)$ is equivalent to a partition function. It can be used to compute thermodynamic quantities such as free energy, entropy, heat capacity and enthalpy [22]. The constant volume heat capacity is obtained using Debye's relation

$$C_v = \sum_j g(\nu_j) k N_A (h\nu_j/kT)^2 \frac{\exp(h\nu_j/kT)}{[\exp(h\nu_j/kT) - 1]^2} \quad (4)$$

with

$$\int g(\nu_j) d\nu_j = 1.$$

The constant volume heat capacity C_v , given by (4) is converted into constant pressure heat capacity C_p using the Nernst–Lindemann approximation [23]

$$C_p - C_v = 3RA_0(C_p^2 T/C_v T_m^2) \quad (5)$$

where A_0 is a constant often of a universal value [3.9×10^{-3} (°K mol)/J] and T_m^2 is the estimated equilibrium melting temperature, which is taken to be 573 °K [4].

3. Results and discussion

In poly(L-leucine) there are 19 atoms per residue unit which give rise to 57 dispersion curves of vibrations. The vibrational frequencies were calculated for the values of δ ranging from 0 to π in steps of 0.05π . Assuming that ψ is the angle of rotation about the helix axis which separates the adjacent units, the modes corresponding to $\delta = 0$ and ψ are infrared as well as Raman active and $\delta = 2\psi$ gives only Raman active modes. Here ψ is the angle of rotation about the helix axis which separates the adjacent units. For α -helical PLL $\psi = 5\pi/9$. The calculated frequencies at $\delta = 0$ and $5\pi/9$ are compared with the observed ones. The force constants which gave best fit to the experimental data are given in table 1. Since the modes above 1350 cm⁻¹ (except amide II) are non-dispersive, only the modes below this are shown in figure 3. Two lowest lying branches ($\delta = 0$ and $\delta = 5\pi/9, \nu = 0$) are the four acoustic modes which correspond to the rotation

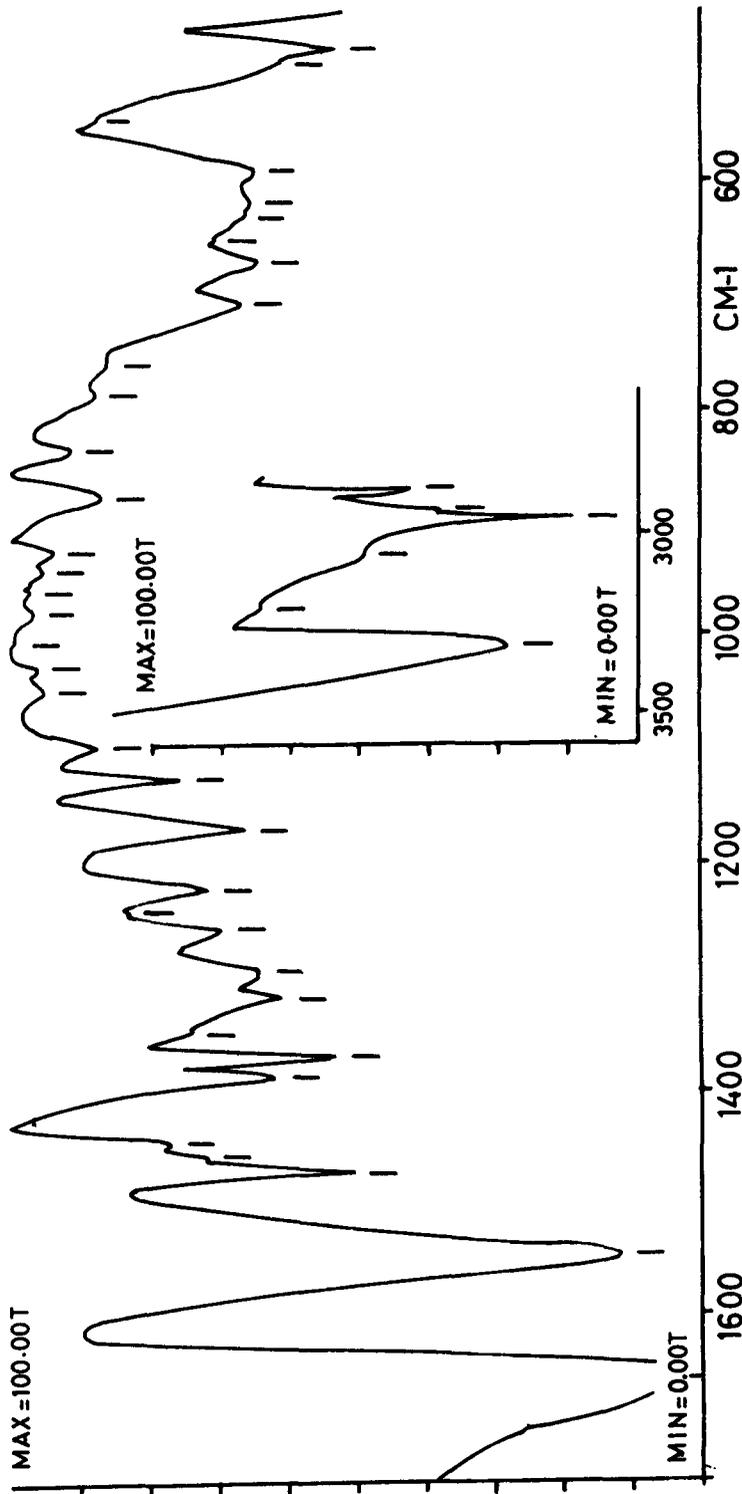


Figure 2(a). F.T.I.R. spectra of poly(L-leucine) (1700–450 cm^{-1}). The region 3500–2750 cm^{-1} is shown in inset.

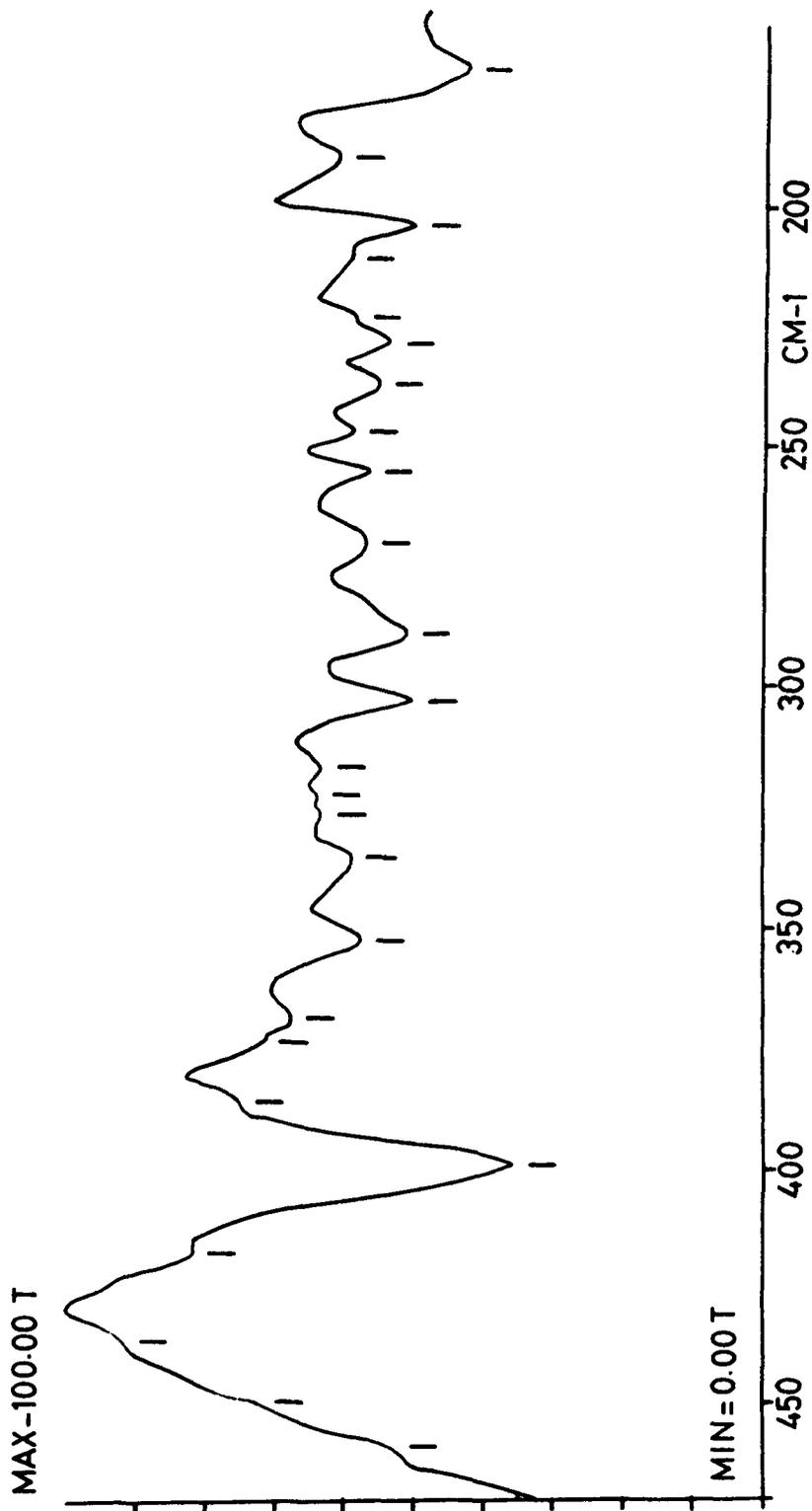


Figure 2(b). F.T.I.R. spectra of poly(L-leucine) (465-150 cm⁻¹).

Table 1. Internal coordinates and force constants (md/Å).

| | | | |
|--|-------|--|-------------|
| $\nu(\text{N}-\text{C}\alpha)$ | 2.850 | $\phi(\text{C}\alpha-\text{C}\beta-\text{C}\gamma)$ | 0.550(0.18) |
| $\nu(\text{C}\alpha-\text{H}\alpha)$ | 4.250 | $\phi(\text{C}\beta-\text{C}\gamma-\text{C}\delta_1)$ | 0.515(0.18) |
| $\nu(\text{C}\alpha-\text{C})$ | 2.700 | $\phi(\text{C}\beta-\text{C}\gamma-\text{C}\delta_2)$ | 0.515(0.18) |
| $\nu(\text{C}=\text{O})$ | 8.300 | $\phi(\text{C}\beta-\text{C}\gamma-\text{H}\gamma)$ | 0.523(0.22) |
| $\nu(\text{C}=\text{N})$ | 6.300 | $\phi(\text{C}\delta_1-\text{C}\gamma-\text{C}\delta_2)$ | 0.515(0.18) |
| $\nu(\text{H}-\text{N})$ | 5.390 | $\phi(\text{C}\delta_1-\text{C}\gamma-\text{H}\gamma)$ | 0.500(0.22) |
| $\nu(\text{C}\alpha-\text{C}\beta)$ | 2.550 | $\phi(\text{C}\delta_2-\text{C}\gamma-\text{H}\gamma)$ | 0.500(0.22) |
| $\nu(\text{H}\beta\beta-\text{C}\beta)$ | 4.250 | $\phi(\text{C}\gamma-\text{C}\delta_1-\text{H}\delta_1)$ | 0.445(0.21) |
| $\nu(\text{H}\beta\alpha-\text{C}\beta)$ | 4.250 | $\phi(\text{C}\gamma-\text{C}\delta_2-\text{H}\delta_2)$ | 0.445(0.21) |
| $\nu(\text{C}\beta-\text{C}\gamma)$ | 2.300 | $\phi(\text{H}\delta_1-\text{C}\delta_1-\text{H}\delta_1)$ | 0.441(0.24) |
| $\nu(\text{C}\gamma-\text{C}\delta_2)$ | 2.120 | $\phi(\text{H}\delta_2-\text{C}\delta_2-\text{H}\delta_2)$ | 0.421(0.24) |
| $\nu(\text{C}\gamma-\text{C}\delta_1)$ | 2.120 | $\phi(\text{C}\alpha-\text{C}\beta-\text{H}\beta\alpha)$ | 0.360(0.20) |
| $\nu(\text{C}\gamma-\text{H}\gamma)$ | 4.340 | $\phi(\text{C}\gamma-\text{C}\beta-\text{H}\beta\beta)$ | 0.360(0.20) |
| $\nu(\text{C}\delta_1-\text{H}\delta_1)$ | 4.330 | $\phi(\text{C}\gamma-\text{C}\beta-\text{H}\beta\alpha)$ | 0.360(0.20) |
| $\nu(\text{C}\delta_2-\text{H}\delta_2)$ | 4.330 | $\phi(\text{C}\alpha-\text{C}\beta-\text{H}\beta\beta)$ | 0.360(0.20) |
| | | $\phi(\text{H}\beta\beta-\text{C}\beta-\text{H}\beta\alpha)$ | 0.422(0.25) |
| $\omega(\text{C}=\text{O})$ | 0.540 | $\phi(\text{N}-\text{C}\alpha-\text{H}\alpha)$ | 0.320(0.80) |
| $\omega(\text{N}-\text{H})$ | 0.120 | $\phi(\text{N}-\text{C}\alpha-\text{C}\beta)$ | 0.450(0.50) |
| | | $\phi(\text{H}\alpha-\text{C}\alpha-\text{C})$ | 0.410(0.20) |
| $\tau(\text{C}-\text{C}\alpha)$ | 0.010 | $\phi(\text{H}\alpha-\text{C}\alpha-\text{C}\beta)$ | 0.410(0.20) |
| $\tau(\text{C}\alpha-\text{C}\beta)$ | 0.050 | $\phi(\text{C}-\text{C}\alpha-\text{C}\beta)$ | 0.520(0.18) |
| $\tau(\text{C}\beta-\text{C}\gamma)$ | 0.080 | $\phi(\text{N}-\text{C}\alpha-\text{C})$ | 0.130(0.50) |
| $\tau(\text{C}\gamma-\text{C}\delta_1)$ | 0.016 | $\phi(\text{C}=\text{N}-\text{C}\alpha)$ | 0.530(0.35) |
| $\tau(\text{C}\gamma-\text{C}\delta_2)$ | 0.016 | $\phi(\text{N}=\text{C}=\text{O})$ | 0.600(0.90) |
| $\tau(\text{C}=\text{N})$ | 0.030 | $\phi(\text{C}=\text{N}-\text{H})$ | 0.200(0.65) |
| $\tau(\text{N}-\text{C}\alpha)$ | 0.010 | $\phi(\text{H}-\text{N}-\text{C}\alpha)$ | 0.427(0.60) |
| | | $\phi(\text{C}\alpha-\text{C}=\text{O})$ | 0.230(0.60) |
| | | $\phi(\text{C}\alpha-\text{C}=\text{N})$ | 0.210(0.60) |

Note: ν , ϕ , ω , τ denote stretch, angle bend, wag and torsion respectively. Non-bonded force constants are given in parentheses.

about the helix axis and the translations \parallel and two \perp to the helix axis. The assignments of modes are made on the basis of potential energy distribution, line intensity, line profile, second derivative spectra and the presence/absence of modes in molecules having atoms placed in similar environment. For the sake of simplicity the modes are discussed under two separate heads viz. backbone modes and side-chain modes.

3.1 Backbone modes

Main-chain of PLL consists of amide groups joined together by $\text{C}\alpha$ atoms. Modes involving the motions of main-chain atoms ($-\text{C}-\text{C}\alpha-\text{N}-$) are termed as backbone modes. Pure back-bone modes are given in table 2 and pure side-chain modes in table 3. The modes involving the coupling of back-bone and side-chain are given in table 4. All the amide modes except amide A and amide I are dispersive. A comparison of various amide modes of α PLL and α poly(L-alanine) [6] is given in table 5. Amide I, II and III modes fall nearly in the same region. It is clear that the frequency of amide

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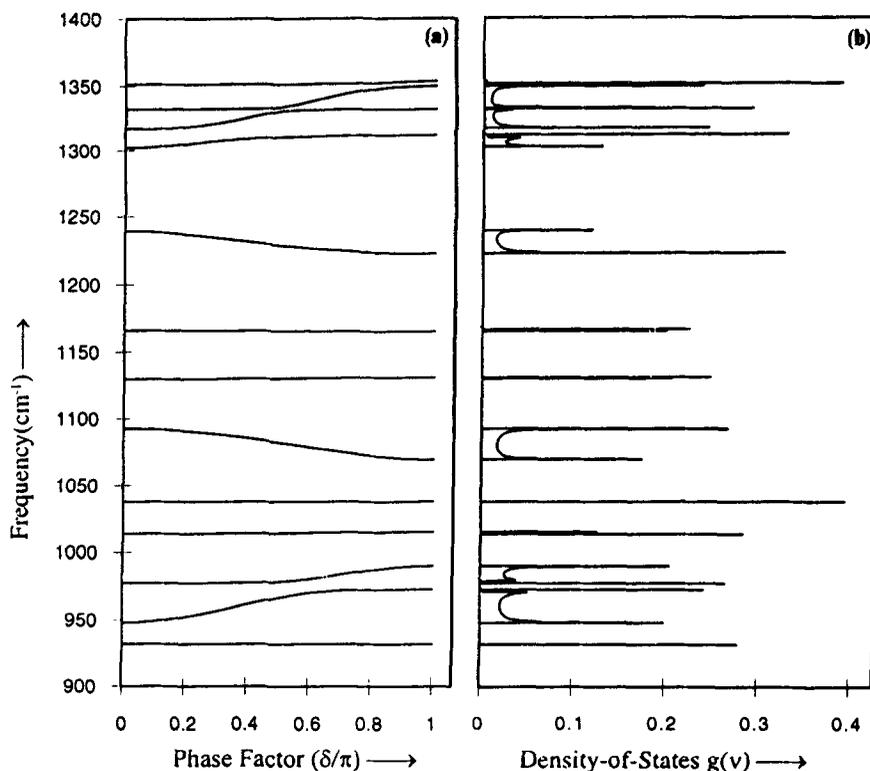


Figure 3. (a) Dispersion curves of poly(L-leucine) ($1400\text{--}900\text{ cm}^{-1}$); (b) Density-of-states $g(\nu)$ ($1400\text{--}900\text{ cm}^{-1}$).

V mode does not depend solely on main-chain conformation but side-chain structure in question also plays an important role in determining the frequency of this mode. The frequency of CO-in-plane-bend (amide IV), CO-out-of-plane bend (amide VI) and C–N torsion (amide VII) are also conformation dependent [24]. These modes mix strongly and very differently with the side-chain coordinates depending on the structure of the main and side-chains. In the spectra of PLL three bands have been observed at 614 , 656 and 703 cm^{-1} . According to Koenig and Sutton [17] these bands are due to amide V in α , disordered and β sheet conformations respectively. The presence of all these modes in the spectra of PLL is said to be indicative of the coexistence of different conformational states. This does not appear to be correct. In α poly(L-alanine) [6] 656 cm^{-1} band has been assigned to amide VI which is calculated in PLL at 647 cm^{-1} . Amide V is calculated at 592 cm^{-1} at $\delta = 0$. On increasing the values of δ contribution of C=O wag increases and at zone boundary it becomes a mixture of amide V and amide VI. The 703 cm^{-1} band is a mixture of side-chain stretches and $\omega(\text{N-H})$. Our assignments are further supported by the fact that these three bands are observed in poly(L- α -amino-n-butyric acid), poly(L-norvaline) and poly(L-norleucine) in α form and on N-deuteration the 703 and 656 cm^{-1} band do not change appreciably in intensities and

Table 2. Pure back-bone modes.

| Cal. | Obs | Assignment (% P.E.D. at $\delta = 0.0$) | Cal. | Obs. | Assignment (% P.E.D. at $\delta = 5\pi/9$) |
|------|------|--|------|------|---|
| 3316 | 3313 | $\nu(\text{H-N})(99)$ | 3316 | 3313 | $\nu(\text{H-N})(99)$ |
| 1662 | 1657 | $\nu(\text{C=O})(57) + \nu(\text{C-N})(32)$ | 1663 | 1657 | $\nu(\text{C=O})(55) + \nu(\text{C=N})(33)$ |
| 1547 | 1546 | $\phi(\text{H-N-C}\alpha)(42) + \phi(\text{C=N-H})(26) + \nu(\text{C=N})(16) + \nu(\text{C}\alpha\text{-C})(5)(26)$ | 1537 | 1518 | $\phi(\text{H-N-C}\alpha)(45) + \phi(\text{C=N-H})(28) + \nu(\text{C=N})(12)$ |
| 1302 | 1299 | $\nu(\text{C=N})(30) + \nu(\text{C=O})(19) + \nu(\text{C}\alpha\text{-C})(12) + \phi(\text{H-N-C}\alpha)(12) + \phi(\text{N=C=O})(8) + \nu(\text{N-C}\alpha)(7)$ | 1311 | 1318 | $\phi(\text{H}\alpha\text{-C}\alpha\text{-C})(7) + \nu(\text{C=N})(5)$ |

Note: All frequencies are given in cm^{-1} .

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Table 3. Pure side-chain modes.

| Cal. | Obs. | Assignments (% P.E.D. at $\delta = 0.0$) |
|------|------|--|
| 2963 | 2960 | $\nu(\text{C}\alpha\text{-H}\alpha)(99)$ |
| 2957 | | $\nu(\text{C}\delta_1\text{-H}\delta_1)(99)$ |
| 2938 | 2938 | $\nu(\text{C}\delta_2\text{-H}\delta_2)(98)$ |
| 2918 | 2916 | $\nu(\text{C}\gamma\text{-H}\gamma)(24) + \nu(\text{C}\delta_1\text{-H}\delta_1)(73)$ |
| 2917 | | $\nu(\text{C}\delta_1\text{-H}\delta_1)(98)$ |
| 2915 | 2913 | $\nu(\text{C}\gamma\text{-H}\gamma)(65) + \nu(\text{C}\delta_1\text{-H}\delta_1)(28)$ |
| 2910 | | $\nu(\text{C}\delta_2\text{-H}\delta_2)(98)$ |
| 2910 | | $\nu(\text{C}\delta_2\text{-H}\delta_2)(96)$ |
| 2906 | 2904 | $\nu(\text{H}\beta\alpha\text{-C}\beta)(47) + \nu(\text{H}\beta\beta\text{-C}\beta)(48)$ |
| 2876 | 2874 | $\nu(\text{H}\beta\beta\text{-C}\beta)(49) + \nu(\text{H}\beta\alpha\text{-C}\beta)(50)$ |
| 1466 | 1471 | $\phi(\text{H}\delta_1\text{-C}\delta_1\text{-H}\delta_1)(92) + \phi(\text{C}\gamma\text{-C}\delta_1\text{-H}\delta_1)(6)$ |
| 1465 | | $\phi(\text{H}\delta_1\text{-C}\delta_1\text{-H}\delta_1)(94)$ |
| 1452 | 1454 | $\phi(\text{H}\delta_2\text{-C}\delta_2\text{-H}\delta_2)(90) + \phi(\text{C}\gamma\text{-C}\delta_2\text{-H}\delta_2)(5)$ |
| 1452 | | $\phi(\text{H}\delta_2\text{-C}\delta_2\text{-H}\delta_2)(93)$ |
| 1444 | 1441 | $\phi(\text{H}\beta\alpha\text{-C}\beta\text{-H}\beta\beta)(76)$ |
| 1393 | 1390 | $\phi(\text{C}\gamma\text{-C}\delta_1\text{-H}\delta_1)(49) + \phi(\text{H}\delta_1\text{-C}\delta_1\text{-H}\delta_1)(45)$ |
| 1380 | 1370 | $\phi(\text{C}\gamma\text{-C}\delta_2\text{-H}\delta_2)(48) + \phi(\text{H}\delta_2\text{-C}\delta_2\text{-H}\delta_2)(45)$ |
| 1351 | 1350 | $\phi(\text{C}\delta_2\text{-C}\gamma\text{-H}\gamma)(49) + \phi(\text{H}\gamma\text{-C}\gamma\text{-C}\delta_1)(24)$ |
| 1333 | 1334 | $\phi(\text{C}\beta\text{-C}\gamma\text{-H}\gamma)(47) + \phi(\text{H}\gamma\text{-C}\gamma\text{-C}\delta_1)(25)$ |
| 1038 | 1040 | $\phi(\text{C}\gamma\text{-C}\delta_1\text{-H}\delta_1)(30) + \phi(\text{C}\gamma\text{-C}\delta_2\text{-H}\delta_2)(22) + \nu(\text{C}\beta\text{-C}\gamma)(11) + \nu(\text{C}\gamma\text{-C}\delta_2)(5) + \phi(\text{C}\delta_2\text{-C}\gamma\text{-C}\delta_1)(6)$ |
| 1014 | 1020 | $\phi(\text{C}\gamma\text{-C}\delta_1\text{-H}\delta_1)(41) + \phi(\text{C}\gamma\text{-C}\delta_2\text{-H}\delta_2)(29)$ |
| 977 | 980 | $\phi(\text{C}\gamma\text{-C}\delta_2\text{-H}\delta_2)(28) + \phi(\text{C}\gamma\text{-C}\delta_1\text{-H}\delta_1)(23) + \nu(\text{C}\gamma\text{-C}\delta_1)(10) + \nu(\text{C}\gamma\text{-C}\delta_2)(7) + \phi(\text{C}\alpha\text{-C}\beta\text{-H}\beta\alpha)(6) + \phi(\text{C}\alpha\text{-C}\beta\text{-H}\beta\alpha)(5)$ |
| 931 | 925 | $\phi(\text{C}\gamma\text{-C}\delta_2\text{-H}\delta_2)(44) + \phi(\text{C}\gamma\text{-C}\delta_1\text{-H}\delta_1)(38)$ |
| 842 | 833 | $\nu(\text{C}\beta\text{-C}\gamma)(35) + \phi(\text{C}\gamma\text{-C}\delta_2\text{-H}\delta_2)(25) + \phi(\text{C}\gamma\text{-C}\delta_1\text{-H}\delta_1)(11) + \nu(\text{C}\gamma\text{-C}\delta_1)(13)$ |
| 830 | | $\nu(\text{C}\gamma\text{-C}\delta_2)(30) + \nu(\text{C}\gamma\text{-C}\delta_1)(20) + \phi(\text{C}\gamma\text{-C}\delta_1\text{-H}\delta_1)(12) + \phi(\text{H}\beta\alpha\text{-C}\beta\text{-C}\gamma)(7) + \phi(\text{C}\gamma\text{-C}\delta_2\text{-H}\delta_2)(7) + \tau(\text{C}\alpha\text{-C}\beta)(6)$ |
| 328 | 323 | $\phi(\text{C}\delta_1\text{-C}\gamma\text{-C}\delta_2)(64) + \phi(\text{C}\beta\text{-C}\gamma\text{-C}\delta_1)(8)$ |
| 282 | 289 | $\tau(\text{C}\gamma\text{-C}\delta_2)(49) + \tau(\text{C}\gamma\text{-C}\delta_1)(48)$ |

Note: All frequencies are in cm^{-1} .

frequencies [18]. Only the band near 610 cm^{-1} shifts to about 450 cm^{-1} because it is due to amide V. One of the interesting features observed in the dispersion curves is the tendency of some curves to crowd or close in near the helix angle, which is indicative of the coupling between various modes. This phenomenon is observed in amide V and amide VI. Amide VI mode is most dispersive (23 cm^{-1}). It has 25% contribution from

Table 4. Mix modes.

| Cal. Obs. | Assignment (% P.E.D. at $\delta = 0.0$) | Cal. Obs. | Assignment (% P.E.D. at $\delta = 5\pi/9$) |
|-----------|---|-----------|---|
| 1317 1318 | $\phi(\text{N-C}\alpha\text{-H}\alpha)(63) + \phi(\text{H}\alpha\text{-C}\alpha\text{-C})(12)$ | 1332 1334 | $\phi(\text{C}\beta\text{-C}\gamma\text{-H}\gamma)(38) + \phi(\text{H}\gamma\text{-C}\gamma\text{-C}\delta_1)(19) + \phi(\text{N-C}\alpha\text{-H}\alpha)(9)$ |
| 1239 1241 | $v(\text{C}\alpha\text{-C})(9) + \phi(\text{H}\alpha\text{-C}\alpha\text{-C})(9) + \phi(\text{H}\alpha\text{-C}\alpha\text{-C}\beta)(18) +$ $v(\text{C}\alpha\text{-C}\beta)(16) + v(\text{C}\beta\text{-C}\gamma)(8) + \phi(\text{C}\alpha\text{-C}\beta\text{-H}\beta\beta)(7) +$ $\phi(\text{H}\beta\beta\text{-C}\beta\text{-C}\gamma)(7) + \phi(\text{C}\alpha\text{-C}\beta\text{-H}\beta\alpha)(6)$ | 1227 1224 | $v(\text{C}\alpha\text{-C}\beta)(16) + \phi(\text{H}\alpha\text{-C}\alpha\text{-C}\beta)(15) + v(\text{C}\beta\text{-C}\gamma)(9) +$ $\phi(\text{H}\alpha\text{-C}\alpha\text{-C}\beta)(9) + \phi(\text{C}\alpha\text{-C}\beta\text{-H}\beta\alpha)(8) + \phi(\text{H}\beta\beta\text{-C}\beta\text{-C}\gamma)(8) +$ $\phi(\text{C}\alpha\text{-C}\beta\text{-H}\beta\beta)(6) + \phi(\text{H}\beta\alpha\text{-C}\beta\text{-C}\gamma)(5)$ |
| 1166 1172 | $\phi(\text{H}\alpha\text{-C}\alpha\text{-C}\beta)(22) + \phi(\text{H}\alpha\text{-C}\alpha\text{-C})(19) +$ $\phi(\text{H}\beta\alpha\text{-C}\beta\text{-C}\gamma)(16) + \phi(\text{C}\alpha\text{-C}\beta\text{-H}\beta\alpha)(10) +$ $\phi(\text{C}\alpha\text{-C}\beta\text{-H}\beta\beta)(8) + v(\text{C}\beta\text{-C}\gamma)(7) + \phi(\text{H}\beta\beta\text{-C}\beta\text{-C}\gamma)(6)$ | 1165 1172 | $\phi(\text{H}\alpha\text{-C}\alpha\text{-C}\beta)(23) + \phi(\text{H}\alpha\text{-C}\alpha\text{-C})(19) + \phi(\text{H}\beta\alpha\text{-C}\beta\text{-C}\gamma)(15)$ $\phi(\text{C}\alpha\text{-C}\beta\text{-H}\beta\alpha)(10) + \phi(\text{C}\alpha\text{-C}\beta\text{-H}\beta\beta)(8) + v(\text{C}\beta\text{-C}\gamma)(6) +$ $\phi(\text{H}\beta\beta\text{-C}\beta\text{-C}\gamma)(6)$ |
| 1130 1130 | $v(\text{N-C}\alpha)(26) + v(\text{C}\alpha\text{-C})(5) + \phi(\text{C}\alpha\text{-C}\beta\text{-H}\beta\alpha)(15) +$ $\phi(\text{C}\alpha\text{-C}\beta\text{-H}\beta\beta)(15) + \phi(\text{H}\beta\alpha\text{-C}\beta\text{-C}\gamma)(9) + \phi(\text{H}\beta\beta\text{-C}\beta\text{-C}\gamma)(5)$ | 1130 1130 | $v(\text{N-C}\alpha)(20) + \phi(\text{C}\alpha\text{-C}\beta\text{-H}\beta\beta)(19) + \phi(\text{C}\alpha\text{-C}\beta\text{-H}\beta\alpha)(16)$ $\phi(\text{H}\beta\beta\text{-C}\beta\text{-C}\gamma)(9) + \phi(\text{H}\beta\alpha\text{-C}\beta\text{-C}\gamma)(9)$ |
| 1093 1099 | $v(\text{N-C}\alpha)(32) + v(\text{C}\alpha\text{-C})(12) + \phi(\text{H}\beta\beta\text{-C}\beta\text{-C}\gamma)(13) +$ $\phi(\text{H}\beta\alpha\text{-C}\beta\text{-C}\gamma)(6)$ | 1080 1076 | $v(\text{N-C}\alpha)(38) + \phi(\text{H}\beta\beta\text{-C}\beta\text{-C}\gamma)(10) + v(\text{C}\alpha\text{-C})(6) +$ $\phi(\text{H}\beta\alpha\text{-C}\beta\text{-C}\gamma)(7)$ |
| 948 943 | $v(\text{C}\alpha\text{-C}\alpha)(5) + \phi(\text{H}\alpha\text{-C}\alpha\text{-C}\beta)(8) + v(\text{C}\alpha\text{-C}\beta)(47) +$ $\phi(\text{C}\gamma\text{-C}\delta_2\text{-H}\delta_2)(5)$ | 969 960 | $v(\text{C}\alpha\text{-C})(7)$ $v(\text{C}\alpha\text{-C}\beta)(17) + \phi(\text{C}\gamma\text{-C}\delta_2\text{-H}\delta_2)(12) + \phi(\text{C}\gamma\text{-C}\delta_1\text{-H}\delta_1)(14) +$ |
| 902 903 | $v(\text{C}\alpha\text{-C})(21) + v(\text{C}=\text{O})(6) + \phi(\text{N}=\text{C}=\text{O})(9) + v(\text{C}=\text{N})(6) +$ $\phi(\text{C}=\text{N-C}\alpha)(6) + \phi(\text{H}\alpha\text{-C}\alpha\text{-C})(5) + \phi(\text{C}\gamma\text{-C}\delta_2\text{-H}\delta_2)(7) +$ $\phi(\text{H}\beta\alpha\text{-C}\beta\text{-C}\gamma)(7) + \phi(\text{C}\gamma\text{-C}\delta_1\text{-H}\delta_1)(6)$ | 896 899 | $v(\text{C}\alpha\text{-C})(16) + v(\text{C}\alpha\text{-C}\beta)(13) + \phi(\text{C}\gamma\text{-C}\delta_2\text{-H}\delta_2)(7) +$ $\phi(\text{H}\beta\alpha\text{-C}\beta\text{-C}\gamma)(6) + \phi(\text{C}\gamma\text{-C}\delta_1\text{-H}\delta_1)(7)$ |
| 875 874 | $\phi(\text{N}=\text{C}=\text{O})(6) + \phi(\text{C}=\text{N-C}\alpha)(6) + v(\text{N-C}\alpha)(6) +$ $\phi(\text{C}\alpha\text{-C}\beta\text{-H}\beta\beta)(9) + \tau(\text{C}\beta\text{-C}\gamma)(6) + \phi(\text{C}\alpha\text{-C}\beta\text{-H}\beta\alpha)(7) +$ $\phi(\text{H}\beta\beta\text{-C}\beta\text{-C}\gamma)(5) + \phi(\text{C}\gamma\text{-C}\delta_1\text{-H}\delta_1)(5) + \phi(\text{C}\gamma\text{-C}\delta_2\text{-H}\delta_2)(5)$ | 873 874 | $\phi(\text{C}\alpha\text{-C}\beta\text{-H}\beta\beta)(10) + v(\text{N-C}\alpha)(7) + \tau(\text{C}\beta\text{-C}\gamma)(6) +$ $\phi(\text{C}\alpha\text{-C}\beta\text{-H}\beta\alpha)(6) + v(\text{C}\alpha\text{-C}\beta)(5) + v(\text{C}\gamma\text{-C}\delta_2)(5) +$ $\phi(\text{C}\gamma\text{-C}\delta_2\text{-H}\delta_2)(5) + \phi(\text{C}\gamma\text{-C}\delta_1\text{-H}\delta_1)(5)$ |
| 734 726 | $\omega(\text{C}=\text{O})(35) + \omega(\text{N-H})(25) + v(\text{C}\gamma\text{-C}\delta_1)(9) + v(\text{C}\gamma\text{-C}\delta_2)(5)$ | 751 756 | $\omega(\text{C}=\text{O})(35) + \omega(\text{N-H})(24) + v(\text{C}\alpha\text{-C}\beta)(8)$ |
| 700 703 | $\omega(\text{N-H})(13) + v(\text{C}\gamma\text{-C}\delta_2)(20) + v(\text{C}\beta\text{-C}\gamma)(19) + v(\text{C}\gamma\text{-C}\delta_1)(14)$ | 699 703 | $v(\text{C}\gamma\text{-C}\delta_2)(25) + v(\text{C}\gamma\text{-C}\delta_1)(23) + v(\text{C}\beta\text{-C}\gamma)(20) + \omega(\text{N-H})(6)$ |
| 647 656 | $\omega(\text{C}=\text{O})(26) + \phi(\text{N-C}\alpha\text{-C})(12) + \phi(\text{C}\alpha\text{-C}\beta\text{-C}\gamma)(8)$ $\{\text{Amide VI}\}$ | 625 633 | $\phi(\text{N}=\text{C}=\text{O})(24) + \omega(\text{C}=\text{O})(10) + \phi(\text{C}\alpha\text{-C}\beta\text{-C}\gamma)(16) +$ $v(\text{N-C}\alpha)(5) + \phi(\text{C}\alpha\text{-C}=\text{O})(5) + \phi(\text{C}\alpha\text{-C}=\text{N})(5) +$ $\phi(\text{C}=\text{N-C}\alpha)(6) + \omega(\text{N-H})(6)$ |

| | | | | | |
|-----|-----|--|-----|-----|--|
| 592 | 587 | $\omega(\text{N-H})(21) + \tau(\text{C=N})(14) + \omega(\text{C=O})(11) + \nu(\text{N-C}\alpha)(6) + \tau(\text{N-C}\alpha)(11) + \phi(\text{N=C=O})(6) + \phi(\text{C-C}\alpha\text{-C}\beta)(5)$ {Amide V + Amide IV} | 603 | 614 | $\omega(\text{N-H})(27) + \omega(\text{C=O})(25) + \tau(\text{C=N})(12) + \tau(\text{N-C}\alpha)(12)$ |
| 549 | 543 | $\phi(\text{C}\alpha\text{-C=N})(16) + \phi(\text{C}\alpha\text{-C=O})(13) + \phi(\text{N-C}\alpha\text{-H}\alpha)(5) + \phi(\text{N-C}\alpha\text{-C}\beta)(19) + \tau(\text{C}\beta\text{-C}\gamma)(7) + \phi(\text{C}\alpha\text{-C}\beta\text{-C}\gamma)(6) + \phi(\text{C}\beta\text{-C}\gamma\text{-C}\delta_2)(5)$ | 501 | 506 | $\phi(\text{N-C}\alpha\text{-C}\beta)(15) + \phi(\text{C}\beta\text{-C}\gamma\text{-C}\delta_2)(10) + \tau(\text{C}\beta\text{-C}\gamma)(9) + \phi(\text{C}\alpha\text{-C=N})(6) + \phi(\text{N-C}\alpha\text{-H}\alpha)(6) + \phi(\text{C}\alpha\text{-C}\beta\text{-C}\gamma)(6) + \nu(\text{N-C}\alpha)(5)$ |
| 412 | 410 | $\phi(\text{C}\alpha\text{-C=O})(10) + \phi(\text{N=C=O})(8) + \nu(\text{C}\alpha\text{-C})(8) + \nu(\text{C}\alpha\text{-C}\beta)(8) + \phi(\text{C}\beta\text{-C}\gamma\text{-C}\delta_2)(7) + \phi(\text{C}\beta\text{-C}\gamma\text{-C}\delta_1)(11) + \phi(\text{C}\beta\text{-C}\gamma\text{-H}\gamma)(7) + \phi(\text{C}\delta_2\text{-C}\gamma\text{-H}\gamma)(7) + \phi(\text{H}\gamma\text{-C}\gamma\text{-C}\delta_1)(7)$ | 438 | 452 | $\phi(\text{C}\beta\text{-C}\gamma\text{-C}\delta_1)(15) + \phi(\text{C}\alpha\text{-C}\beta\text{-C}\gamma)(8) + \nu(\text{C}\alpha\text{-C})(7) + \nu(\text{C}\alpha\text{-C}\beta)(6) + \phi(\text{C}\beta\text{-C}\gamma\text{-C}\delta_2)(7) + \phi(\text{C}\delta_2\text{-C}\gamma\text{-H}\gamma)(6) + \phi(\text{C}\alpha\text{-C=O})(6) + \phi(\text{C}\beta\text{-C}\gamma\text{-H}\gamma)(5)$ |
| 388 | 399 | $\phi(\text{C}\alpha\text{-C=O})(9) + (\text{C}\alpha\text{-C=N})(5) + \tau(\text{C}\beta\text{-C}\gamma)(8) + \phi(\text{C}\beta\text{-C}\gamma\text{-C}\delta_1)(26) + \phi(\text{C}\beta\text{-C}\gamma\text{-C}\delta_2)(20) + \tau(\text{C}\alpha\text{-C}\beta)(11)$ | 372 | 368 | $\phi(\text{C}\beta\text{-C}\gamma\text{-C}\delta_1) + \phi(\text{C}\beta\text{-C}\gamma\text{-C}\delta_2)(16) + \phi(\text{C}\alpha\text{-C=O})(10) + \phi(\text{C}\alpha\text{-C=N}) + \tau(\text{C}\alpha\text{-C}\beta)(5)$ |
| 300 | 302 | $\phi(\text{C=N-C}\alpha)(10) + \phi(\text{N=C=O})(13) + \phi(\text{C}\alpha\text{-C=O})(6) + \phi(\text{C-C}\alpha\text{-C}\beta)(8) + \tau(\text{C}\gamma\text{-C}\delta_2)(17) + \tau(\text{C}\gamma\text{-C}\delta_1)(15)$ | 310 | 317 | $\tau(\text{C}\gamma\text{-C}\delta_2)(13) + \phi(\text{C=N-C}\alpha)(11) + \tau(\text{C}\gamma\text{-C}\delta_1)(11)$ $\phi(\text{N-C}\alpha\text{-C})(10) + \phi(\text{N=C=O})(8) + \phi(\text{C}\alpha\text{-C=O})(7) + \phi(\text{C-C}\alpha\text{-C}\beta)(6)$ |
| 268 | 271 | $\phi(\text{N=C=O})(5) + \phi(\text{C=N-C}\alpha)(6) + \phi(\text{C-C}\alpha\text{-C}\beta)(5) + \tau(\text{C}\gamma\text{-C}\delta_1)(32) + \tau(\text{C}\gamma\text{-C}\delta_2)(29)$ | 271 | 271 | $\tau(\text{C}\gamma\text{-C}\delta_2)(37) + \tau(\text{C}\gamma\text{-C}\delta_1)(33)$ |
| 217 | 227 | $\phi(\text{N-C}\alpha\text{-C})(22) + \tau(\text{C=N})(11) + \tau(\text{C-C}\alpha)(7) + \phi(\text{C=N-C}\alpha)(6) + \tau(\text{N-C}\alpha)(5) + \phi(\text{C}\alpha\text{-C=O})(5) + \phi(\text{C-C}\alpha\text{-C}\beta)(8)$ {Amide VII} | 240 | 246 | $\phi(\text{N-C}\alpha\text{-C}\beta)(23) + \phi(\text{C}\beta\text{-C}\gamma\text{-C}\delta_2)(22) + \phi(\text{C}\alpha\text{-C=N})(7) + \phi(\text{C}\alpha\text{-C=O})(5) + \phi(\text{N=C=O})(5) + \phi(\text{N-C}\alpha\text{-C})(6)$ |
| 195 | 189 | $\phi(\text{C-C}\alpha\text{-C}\beta)(19) + \phi(\text{N-C}\alpha\text{-C}\beta)(12) + \phi(\text{C}\beta\text{-C}\gamma\text{-C}\delta_2)(15) + \tau(\text{C}\beta\text{-C}\gamma)(17) + \tau(\text{C}\alpha\text{-C}\beta)(5)$ | 136 | 144 | $\tau(\text{C=N})(7) + \tau(\text{C-C}\alpha)(7) + \phi(\text{C}\beta\text{-C}\gamma\text{-C}\delta_2)(6)$ $\phi(\text{C}\alpha\text{-C}\beta\text{-C}\gamma)(24) + \phi(\text{C}\beta\text{-C}\gamma\text{-C}\delta_1)(14) + \tau(\text{C}\beta\text{-C}\gamma)(6)$ |
| 148 | 144 | $\phi(\text{C}\alpha\text{-C=N})(9) + \phi(\text{C}\alpha\text{-C}\beta\text{-H}\beta\alpha)(6) + \phi(\text{C}\alpha\text{-C}\beta\text{-H}\beta\beta)(5) + \phi(\text{C}\beta\text{-C}\gamma\text{-C}\delta_2)(8) + \phi(\text{C}\beta\text{-C}\gamma\text{-C}\delta_1)(19) + \tau(\text{C}\beta\text{-C}\gamma)(17) + \tau(\text{C}\alpha\text{-C}\beta)(5)$ | 109 | 104 | $\phi(\text{C-C}\alpha\text{-C}\beta)(26) + \phi(\text{N-C}\alpha\text{-C})(9) + \phi(\text{C=N-C}\alpha)(6) + \tau(\text{C-C}\alpha)(6) + \tau(\text{C}\beta\text{-C}\gamma)(7) + \omega(\text{C=O})(5)$ |
| 98 | — | $\phi(\text{C=N-C}\alpha)(5) + \phi(\text{C-C}\alpha\text{-C}\beta)(14) + \phi(\text{C}\alpha\text{-C}\beta\text{-C}\gamma)(40)$ | | | |

(Continued)

Table 4. (Continued)

| Cal. | Obs. | Assignment (% P.E.D. at $\delta = 0.0$) | Cal. | Obs. | Assignment (% P.E.D. at $\delta = 5\pi/9$) |
|------|------|---|------|------|--|
| 79 | — | $\tau(\text{C-C}\alpha)(11) + \phi(\text{C=N-C}\alpha)(6) + \phi(\text{N-C}\alpha\text{-C}\beta)(17) + \tau(\text{C}\beta\text{-C}\gamma)(25) + \tau(\text{C}\alpha\text{-C}\beta)(15)$ | 87 | — | $\phi(\text{N-C}\alpha\text{-C}\beta)(13) + \phi(\text{C}\alpha\text{-C}\beta\text{-C}\gamma)(16) + \tau(\text{C}\beta\text{-C}\gamma)(12) + \tau(\text{C-C}\alpha)(11) + \phi(\text{C}\alpha\text{-C}\beta\text{-H}\beta\beta)(6) + \tau(\text{C}\alpha\text{-C}\beta)(5)$ |
| 63 | 65 | $\tau(\text{C-C}\alpha)(26) + \tau(\text{C=N})(6) + \tau(\text{N-C}\alpha)(23) + \phi(\text{N-C}\alpha\text{-C})(9) + \phi(\text{N-C}\alpha\text{-C}\beta)(9) + \phi(\text{C}\alpha\text{-C}\beta\text{-C}\gamma)(8)$ | 60 | 65 | $\tau(\text{C}\alpha\text{-C}\beta)(29) + \tau(\text{N-C}\alpha)(11) + \tau(\text{C-C}\alpha)(10) + \tau(\text{C}\beta\text{-C}\gamma)(8) + \omega(\text{N-H})(5)$ |
| 39 | — | $\phi(\text{C}\alpha\text{-C=N})(13) + \phi(\text{H}\alpha\text{-C}\alpha\text{-C})(7) + \phi(\text{C=N-C}\alpha)(6) + \phi(\text{N-C}\alpha\text{-C}\beta)(8) + \tau(\text{C}\alpha\text{-C}\beta)(34)$ | 40 | — | $\tau(\text{C}\alpha\text{-C}\beta)(14) + \tau(\text{C=N})(12) + \tau(\text{C-C}\alpha)(10) + \tau(\text{N-C}\alpha)(9) + \phi(\text{N-C}\alpha\text{-C}\beta)(8) + \phi(\text{C}\alpha\text{-C=N})(8) + \phi(\text{C-C}\alpha\text{-C}\beta)(6) + \phi(\text{C}\alpha\text{-C}\beta\text{-C}\gamma)(5)$ |

Note: All frequencies are in cm^{-1} .

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Table 5. Comparison of amide modes of poly-L-leucine and poly-L-alanine.

| | Poly-L-leucine | | Poly-L-alanine | |
|-----------|----------------|-------------------|----------------|-------------------|
| | $\delta = 0.0$ | $\delta = 5\pi/9$ | $\delta = 0.0$ | $\delta = 5\pi/9$ |
| Amide A | 3313 | 3313 | 3293 | 3293 |
| Amide I | 1657 | 1657 | 1659 | 1659 |
| Amide II | 1546 | 1518 | 1515 | 1540 |
| Amide III | 1299 | 1318 | 1270 | 1274 |
| Amide IV | 587 | 633 | 525 | 440 |
| Amide V | 587 | 617 | 595 | 610 |
| Amide VI | 656 | 633 | 685 | 656 |
| Amide VII | 227 | 171 | 238 | 190 |

Note: All frequencies are given in cm^{-1} .

$\omega(\text{C}=\text{O})$. With increase in δ , the energy of this mode and the contribution of $\omega(\text{C}=\text{O})$ decrease whereas $\phi(\text{O}=\text{C}=\text{N})$ and $\omega(\text{N}-\text{H})$ start mixing. At $\delta = \psi$ it becomes a mixture of amide IV and V. This characteristic feature has also been noticed in α poly(L-alanine) [6] and poly(α -aminoisobutyric acid) [15] (3_{10} helix) and can be attributed to strong intramolecular interactions stabilizing the helical structure. The dispersion curves of polyglycine II and other β sheet samples do not show this feature [7, 8]. The observed peak at 227 cm^{-1} has been assigned to amide VII and this mode has a lower value at $\delta = 5\pi/9$ in comparison to $\delta = 0$. The P.E.D. of this mode shows considerable mixing with $\text{C}\alpha-\text{N}$ and $\text{C}\alpha-\text{C}$ torsions. As in case of α poly(L-alanine) [6], in α PLL also, there is certain amount of mixing of the torsional modes with the angle bending modes. The peak at 543 cm^{-1} has been assigned to the mixture of ($\text{N}-\text{C}\alpha-\text{C}\beta$) bend (junction mode) and main-chain deformation. This mode shows maximum dispersion (64 cm^{-1}).

3.2 Side-chain modes

The side-chain $[-\text{CH}_2\text{CH}(\text{CH}_3)_2]$ of PLL consists of a CH_2 attached to a gem dimethyl group. Pure side-chain modes are given in table 3. The CH_2 scissoring mode calculated at 1444 cm^{-1} corresponds to the observed band at 1441 cm^{-1} in PLL and at 1453 cm^{-1} in poly(γ -benzyl-L-glutamate) [17].

The peaks at 1334 , 1318 and 1299 cm^{-1} have been assigned to ($\text{C}\gamma-\text{H}\gamma$) bend, ($\text{C}\alpha-\text{H}\alpha$) bend and amide III (back-bone mode) respectively. With increase in δ the contribution of ($\text{C}\gamma-\text{H}\gamma$) and ($\text{C}\alpha-\text{H}\alpha$) bend decrease in 1334 cm^{-1} and 1318 cm^{-1} mode respectively and the latter one starts mixing with the amide III. A repulsion takes place between 1334 and 1318 cm^{-1} modes in the neighbourhood of helix angle and at the point of inflexion there is a sudden jump in the density-of-states.

The observed band at 1172 cm^{-1} has been tentatively assigned to rocking of CH_3 group by Koenig and Sutton [17] but according to our normal mode calculations this mode is a mixture of ($\text{C}\alpha-\text{H}\alpha$) bend (40%) and CH_2 wag (25%). This is further supported by the fact that in poly(γ -benzyl-L-glutamate) which does not have any methyl group, the observed Raman band at 1183 cm^{-1} has been assigned to CH_2 wag

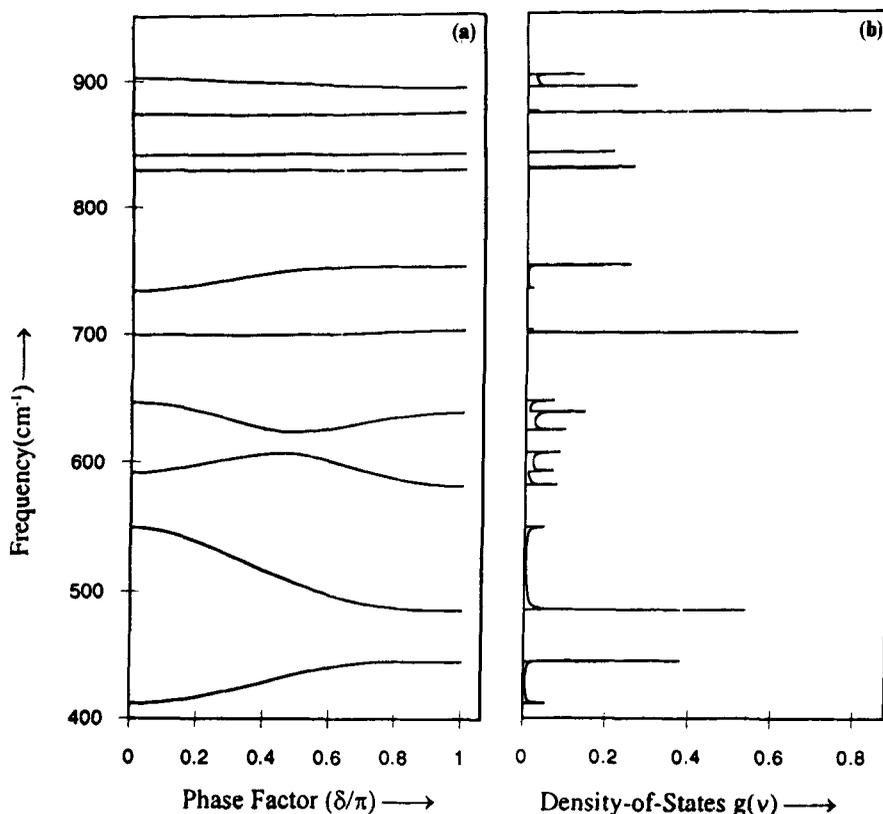


Figure 4. (a) Dispersion curves of poly(L-leucine) ($950\text{--}400\text{ cm}^{-1}$); (b) Density-of-states $g(\nu)$ ($950\text{--}400\text{ cm}^{-1}$).

[17]. This is consistent with our assignment. The CH_2 rocking mode is assigned to the peak at 875 cm^{-1} which is in accordance with the assignment of Koenig and Sutton [17]. All pure side chain modes are non-dispersive.

The modes calculated at 1130 and 1093 cm^{-1} ($\delta = 0$) correspond to the observed peaks at 1129 and 1099 cm^{-1} . They contain a mixture of side-chain CH_2 twist and skeletal ($\text{N-C}\alpha$) stretch. The 1130 cm^{-1} mode is non-dispersive. At $\delta = 0$ it has 34% contribution from CH_2 twist and as δ increases the contribution of ($\text{N-C}\alpha$) stretch decreases and that of CH_2 twist increases. The other one (1099 cm^{-1}) has 13% contribution from CH_2 twist (at $\delta = 0$) and shows a reverse behaviour later on. This mode is dispersive and with increase in δ the contribution of ($\text{N-C}\alpha$) stretch increases and that of CH_2 twist decreases. The modes at 948 and 1038 cm^{-1} (at $\delta = 0$) are mixtures of CH_3 rock and side-chain (C-C) stretch. The 1038 cm^{-1} mode is non-dispersive and has very little contribution from side-chain ($\text{C}\beta\text{--C}\gamma$) stretch. The other one (948 cm^{-1}) has 47% contribution from side-chain ($\text{C}\alpha\text{--C}\beta$) stretch (at $\delta = 0$). In the 948 cm^{-1} mode the contribution of ($\text{C}\alpha\text{--C}\beta$) stretch decreases and that of CH_3 rock, ($\text{C}\gamma\text{--C}\delta_2$) and ($\text{C}\gamma\text{--C}\delta_1$) stretches increase with increase in δ and the frequency of this

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mode increases and in the neighbourhood of helix angle ($\delta = \psi$) it exchanges its character with the 977 cm^{-1} mode (CH_3 rock at $\delta = 0$). After this, the 948 cm^{-1} mode becomes non-dispersive and 977 cm^{-1} mode is repelled upwards. They belong to the same symmetry species [25].

3.3 Specific heat

Recently, heat capacity measurements for a series of polyamino acids have been reported by Roles *et al* [3–4]. Their approach basically involves separation of vibrational spectra into group and skeletal spectrum and obtaining the number of vibrators for each case. These are obtained from the dispersion curves and spectra of polymers having the same skeletal structure (e.g. poly(L-glycine) and α poly(L-alanine) for poly(L-leucine)). As remarked earlier this approach has its own limitations specially when the back-bone and side-chain modes are heavily mixed up. This is very true in case of poly(L-leucine) below 1200 cm^{-1} . The density-of-states are shown in figures 3(b), 4(b) and 5(b). Modes which are purely skeletal, purely side-chain and mixture of

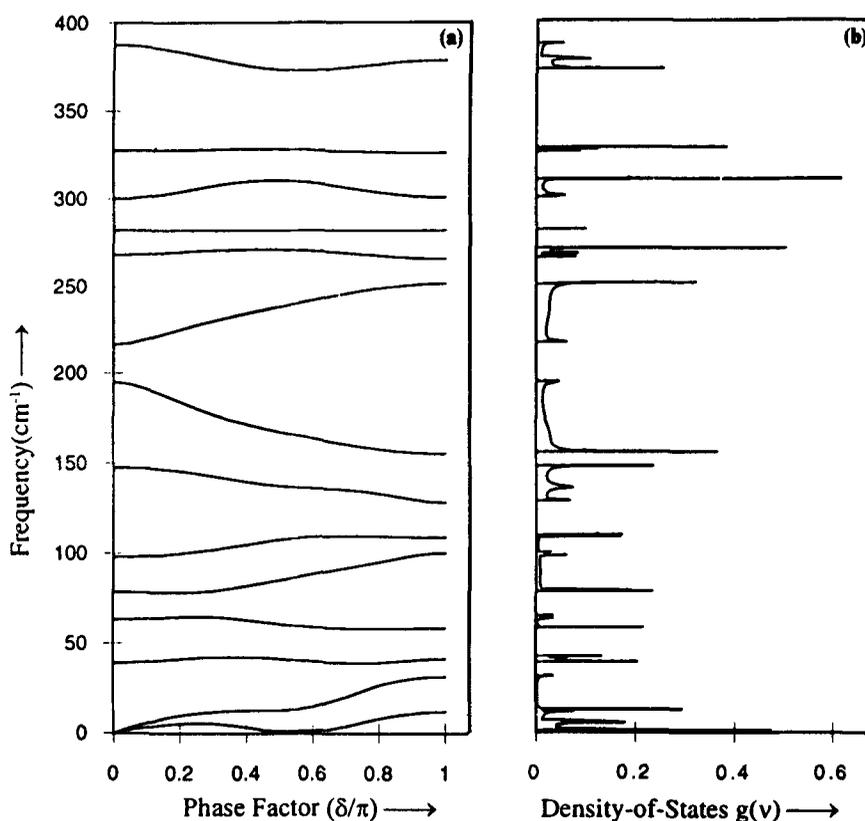


Figure 5. (a) Dispersion curves of poly(L-leucine) below 500 cm^{-1} , (b) Density-of-states $g(\nu)$ below 500 cm^{-1} .

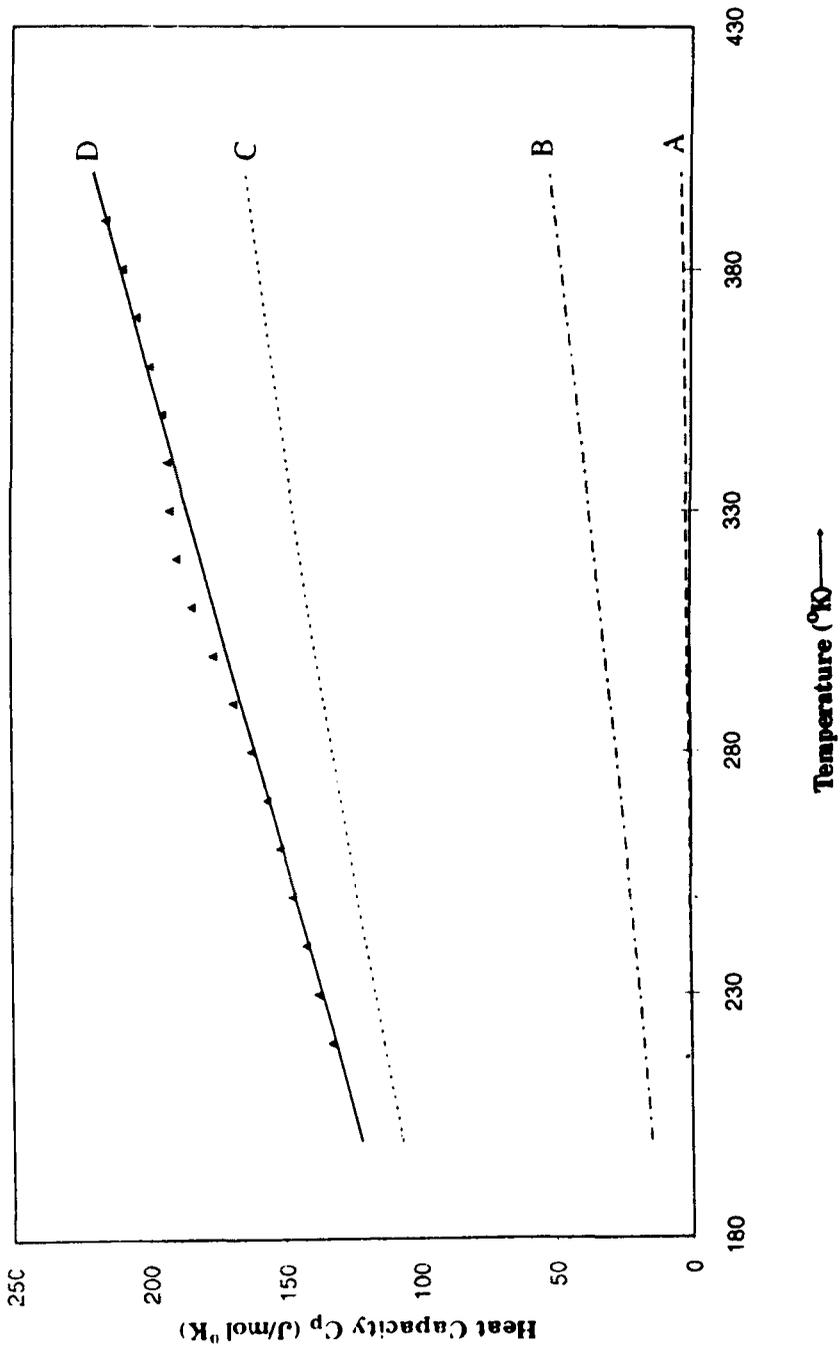


Figure 6. Variation of heat capacity C_p with temperature. [The contribution of back-bone modes (---), side-chain modes (---), mixed modes (- - -) and total heat capacity (—) are shown by curves A, B, C and D respectively. \blacktriangle represents the experimental data].

Heat capacity and phonons in poly(L-leucine)

these two are given in tables 2, 3 and 4 respectively. Their contributions to the heat capacities are shown in figure 6A, 6B and 6C respectively in the temperature range 220–390 K. Total heat capacity is shown in figure 6D and Δ 's represent the experimental data of Roles *et al* [4]. The calculations are in very good agreement with the experimental measurements except in the region 300–330 K wherein experimental data show a bump. Although not explicitly mentioned, this bump could be due to some artifacts in experiments, such as presence of moisture. It should disappear on repeating measurements. Presence of any glass type transition is also not reported. Our methodology gives better agreement with experimental data substantiated by the r.m.s. deviation value which is 0.83% as compared with 1.09% of Roles *et al* [4].

The contribution from the lattice modes is bound to make an appreciable difference to the specific heat because of its sensitivity to these modes. At the moment, the calculation for dispersion curves for a unit cell are extremely difficult because even if we assume a minimum of two chains in unit cell then there would be 180 atoms leading to a matrix of 540×540 . It would bring in an enormous number of interactions and make the problem almost intractable. Thus in spite of several limitations involved in the calculation of specific heat, the present work does provide a good starting point for further basic studies on thermodynamical behaviour of polypeptides and proteins which go into well-defined conformations.

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