Density Functional Theory; a New Route for Structural and Thermodynamic Parameters Calculations

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Abstract

Structural and thermodynamic parameters of the studied virgin polymeric matrices poly ε-caprolactone (PCL), Chitosan (Chi) and their polymer blend were investigated using theoretical density functional theory (DFT). Thermodynamic functions were calculated based on vibrational frequencies and optimized geometrical coordinates in the temperature range 25-1000 °K which cannot be amended easily. Calculated free energy was found to be convex in terms of extensive variable and concave in terms of intensive ones.

Keywords: Density functional theory (DFT); Thermodynamic parameters; Free energy; Entropy; Specific heat.

1. Introduction

Physical and thermodynamic parameters of solids are attributable to their structural arrangement and also to the internal energy of their complexes. Experimental measurement of such structural parameters are limited due to the expenses and facilities that can give results with accurate precision. Polymer blends are composed of two or more organic polymer matrices. Due to the unsatisfactory thermal, mechanical and electric properties, there is a need to functionalize them in an attempt to improve their properties to extend their potential applications [1, 2]. Chitosan (Chi) is obtained from chitin, the second most abundant polysaccharide in nature, which is found in the exoskeletons of crustaceans such as crab and shrimp [3]. Chitin comprises of a linear chain of N-acetyl D-glucosamine molecules. Deacetylation of chitin to various degrees (typically 60-95%) in hot concentrated alkali removes the acetyl groups and forms chitosan. Therefore, chitosan may be considered as a copolymer of D-glucosamine and N-acetyl Dglucosamine residues where the relative ratio of D-glucosamine to N-acetyl-Dglucosamine represents the degree of deacetylation of chitosan. The chemical structure of chitosan has been investigated by Fourier Transform Infrared Spectroscopy (FTIR) in which functional groups of a molecule absorb infrared radiation at specific wavenumbers. FTIR of chitosan shows the amine and hydroxyl functional groups which show overlapping peaks in 3300-3500 cm\(^{-1}\) [3-5]. The degradation rate is dependent on several factors including MW, DD, local pH, temperature, structural stability and homogeneity of source [6-8]. Poly(ε-caprolactone) (PCL) is one of the most flexible and easy to process polymers, but also one of the slowest degrading ones [9]. This could be achieved by mixing chitosan and PCL for their unique contribution to the necessary biomechanical properties. However, chemical reactions such as copolymerization or crosslinking between chitosan and PCL may compromise their individual properties. Therefore, an ideal option is to make the polymeric components co-exist by mixing them physically. Physical mixing can be done by dissolution in a common solvent. However, there is a lack of common solvent for chitosan and PCL as they are hydrophilic and hydrophobic by nature, respectively. Chitosan and PCL mixtures present a model system for studying composites of two semi-crystalline polymers that differ in charge distribution, as chitosan is cationic in nature and PCL is uncharged. Blending two polymers is an approach to develop new biomaterials exhibiting combinations of properties that could not be obtained by individual polymers and to develop a new composite biomaterial that can be fabricated into thin films with alterable mechanical [10], biological and degradation properties for the regeneration of a variety of soft tissues [11]. The hypothesis of this work is that chitosan and PCL are versatile polymers with mutually complementary biomechanical properties and combining them would result in a unique biomaterial that can be fabricated into three-dimensional constructs with tunable physicochemical and biomechanical properties for a wide range of tissue engineering applications. As a modern technique of physics, Computational molecular modeling has greatly accelerated success in the determination of structural parameters, vibrational frequencies, and also
thermodynamic properties of complexes. It is started in the last several decades and improvements in the 
computing power help physicist to predict thermodynamics of polymeric systems which is difficult to be 
measured experimentally. Determination of the thermodynamic quantities from experiments is always 
constrained by the particular technique used, and it may difficult to compare quantities derived from different 
techniques.

2. Materials and Methods

Selected polymeric material including poly \( \varepsilon \)-caprolactone (PCL), Chitosan (Chi) and their semi-natural 
polymer blend with a huge number of applications were studied theoretically for their atomic arrangement, 
interaction and their thermodynamic parameters. The efficient density functional theory (DFT) was applied to 
determine the structural parameters and thermodynamic parameters.

Studied thermodynamic functions of selected materials were calculated on the base of optimized 
geometrical coordinates for temperature interval between 25−1000 K. DFT/B3LYP method was applied for the 
calculations of the equilibrium geometrical and thermodynamic parameters of chitosan, PCL and their blend.

3. Formalism of thermodynamics quantities

For a free energy \( F \), the condition of stability must be slightly amended, as it was generated from the 
energy using a Legendre transform. For an extensive variable \( X \), the stability condition is identical to that 
of the energy,

\[
\frac{\partial^2 F}{\partial X^2} \geq 0, 
\]

(1)

and the free energy is convex in \( X \). However, for intensive variables \( x \), the free energy is concave in \( x \):

\[
\frac{\partial^2 F}{\partial x^2} \leq 0
\]

(2)

The first derivatives of the free energies have been previously given a physical meaning. The second 
derivatives also have physical meaning for certain free energies, and in these contexts they are known as 
"susceptibilities". Two important susceptibilities are the heat capacity \( C_p \), which is an extensive measure of 
the heat flow necessary to change temperature,

\[
C \equiv \frac{\delta Q}{\delta T} = T \frac{ds}{dt},
\]

(3)

and the bulk modulus \( K \), an intensive measure of the change in pressure upon expansion/contraction of 
the system,

\[
K \equiv -\nu \frac{dp}{dV}.
\]

(4)

Both equations (3,4) assume a particular process is being carried out, the former that temperature is 
changing and the later that volume is changing, but knowledge of the other constrained variable are 
necessary to convert these into proper thermodynamic quantities. It is usually assumed that particle
number is fixed, so the heat capacity may be evaluated at fixed pressure $C_p$ or fixed volume $C_V$, and the bulk modulus may be evaluated at fixed temperature $K_T$ or fixed entropy $K_S$. Each quantity suggests a natural ensemble,

$$K_T = V \frac{\partial^2 A}{\partial V^2} \{N_i\}$$  \hspace{1cm} (5)$$
$$K_S = V \frac{\partial^2 U}{\partial V^2} \{S_i\}$$ \hspace{1cm} (6)$$
$$C_V = -T \frac{\partial^2 A}{\partial T^2} \{V_i\}$$ \hspace{1cm} (7)$$
$$C_P = -T \frac{\partial^2 G}{\partial T^2} \{P_i\}$$ \hspace{1cm} (8)$$

The stability requires all four of these quantities to be positive, and the specific heat and bulk modulus must always be non-negative.
4. Results and Discussion

DFT route can be used to perform calculations without fitted parameters, so, it is a power tool to examine the polymeric materials. It predicts the structures stability in the infinite time and volume. DFT route also can provide energy optimization of the three dimensional network of solid material unit structure.

Optimized three dimensional polymeric network of the studied solid material Chi, PCL and their suggested interaction counterpart can be shown in Figure (1, a-c). Calculated values of molar heat capacity $C_p$, Gibbs reduced free energy $\Phi$, entropy $S$ and enthalpy increment $H(T) - H(0)$ corresponding to this optimized structures are listed in Tables (1-3) for Chitosan, PCL, and their blend respectively.

![Optimized structure of Chitosan](image1)

![Optimized structure of PCL](image2)

![Optimized structure of PCL/Chi blend](image3)

Figure 1 Optimized structure of studied polymeric materials
Table (1): The thermodynamics properties of chitosan.

| T(K) | Cp     | S      | ϕ      | H(T)-H(O) |
|------|--------|--------|--------|-----------|
|      | (J.mol⁻¹.K⁻¹) | (J.mol⁻¹.K⁻¹) | (J.mol⁻¹.K⁻¹) | (kJ.mol⁻¹) |
| 25   | 21.743 | 71.701 | 354.108 | 355.901   |
| 50   | 38.125 | 92.024 | 352.056 | 356.657   |
| 75   | 51.906 | 110.132| 349.526 | 357.786   |
| 100  | 64.917 | 126.858| 346.561 | 359.247   |
| 125  | 77.504 | 142.703| 343.19  | 361.028   |
| 150  | 89.715 | 157.918| 339.431 | 363.119   |
| 175  | 101.661| 172.647| 335.298 | 365.511   |
| 200  | 113.47 | 186.994| 330.802 | 368.201   |
| 225  | 125.222| 201.038| 325.951 | 371.184   |
| 250  | 136.932| 214.838| 320.752 | 374.461   |
| 275  | 148.557| 228.435| 315.211 | 378.03    |
| 298.15 | 159.182| 240.867| 309.778 | 381.593   |
| 300  | 160.023| 241.854| 309.332 | 381.888   |
| 325  | 171.246| 255.108| 303.119 | 386.029   |
| 350  | 182.146| 268.2  | 296.578 | 390.448   |
| 375  | 192.659| 281.127| 289.711 | 395.134   |
| 400  | 202.736| 293.885| 282.523 | 400.077   |
| 425  | 212.35 | 306.467| 275.018 | 405.266   |
| 450  | 221.487| 318.866| 267.201 | 410.69    |
| 475  | 230.147| 331.075| 259.076 | 416.337   |
| 500  | 238.341| 343.09 | 250.649 | 422.194   |
| 525  | 246.085| 354.908| 241.923 | 428.25    |
| 550  | 253.402| 366.527| 232.905 | 434.495   |
| 575  | 260.314| 377.945| 223.599 | 440.917   |
| 600  | 266.848| 389.163| 214.009 | 447.507   |
| 625  | 273.029| 400.183| 204.142 | 454.256   |
|   |       |       |       |       |
|---|-------|-------|-------|-------|
| 650| 278.88| 411.006| 194.002| 461.156|
| 675| 284.427| 421.636| 183.594| 468.198|
| 700| 289.689| 432.076| 172.922| 475.375|
| 725| 294.689| 442.329| 161.991| 482.68|
| 750| 299.444| 452.401| 150.807| 490.107|
| 775| 303.97| 462.294| 139.373| 497.65|
| 800| 308.285| 472.013| 127.694| 505.304|
| 825| 312.401| 481.563| 115.774| 513.063|
| 850| 316.332| 490.948| 103.617| 520.923|
| 875| 320.09| 500.172| 91.227| 528.878|
| 900| 323.684| 509.24| 78.609| 536.926|
| 925| 327.124| 518.156| 65.767| 545.061|
| 950| 330.42| 526.924| 52.703| 553.281|
| 975| 333.579| 535.548| 39.422| 561.581|
|1000| 336.608| 544.032| 25.927| 569.958|
Table (2): The thermodynamics properties of PCL.

| T(K) | Cp   | S    | φ    | H(T)-H(O)  |
|------|------|------|------|------------|
|      | (J.mol⁻¹.K⁻¹) | (J.mol⁻¹.K⁻¹) | (J.mol⁻¹.K⁻¹) | (kJ.mol⁻¹) |
| 25   | 8.72 | 49.831 | 108.212 | 109.458    |
| 50   | 11.211 | 56.627 | 106.875 | 109.707    |
| 75   | 13.667 | 61.642 | 105.395 | 110.018    |
| 100  | 15.928 | 65.889 | 103.799 | 110.388    |
| 125  | 18.032 | 69.671 | 102.104 | 110.813    |
| 150  | 20.079 | 73.14 | 100.318 | 111.289    |
| 175  | 22.151 | 76.39 | 98.449 | 111.817    |
| 200  | 24.3 | 79.487 | 96.5 | 112.398    |
| 225  | 26.551 | 82.478 | 94.476 | 113.033    |
| 250  | 28.906 | 85.396 | 92.377 | 113.726    |
| 275  | 31.35 | 88.265 | 90.206 | 114.479    |
| 298.15 | 33.669 | 90.892 | 88.132 | 115.232    |
| 300  | 33.856 | 91.1 | 87.964 | 115.294    |
| 325  | 36.393 | 93.91 | 85.651 | 116.172    |
| 350  | 38.931 | 96.7 | 83.269 | 117.114    |
| 375  | 41.442 | 99.472 | 80.816 | 118.118    |
| 400  | 43.904 | 102.226 | 78.295 | 119.185    |
| 425  | 46.302 | 104.96 | 75.705 | 120.313    |
| 450  | 48.623 | 107.672 | 73.047 | 121.5      |
| 475  | 50.861 | 110.361 | 70.322 | 122.744    |
| 500  | 53.012 | 113.025 | 67.53 | 124.042    |
| 525  | 55.075 | 115.662 | 64.671 | 125.393    |
| 550  | 57.052 | 118.27 | 61.747 | 126.795    |
| 575  | 58.946 | 120.848 | 58.758 | 128.245    |
| 600  | 60.758 | 123.396 | 55.704 | 129.742    |
| 625  | 62.494 | 125.911 | 52.588 | 131.283    |
| 650  | 64.156 | 128.395 | 49.409 | 132.866    |
| 675 | 65.75 | 130.846 | 46.169 | 134.49 |
| 700 | 67.277 | 133.265 | 42.867 | 136.153 |
| 725 | 68.743 | 135.652 | 39.506 | 137.853 |
| 750 | 70.15 | 138.006 | 36.085 | 139.59 |
| 775 | 71.501 | 140.329 | 32.606 | 141.36 |
| 800 | 72.8 | 142.619 | 29.069 | 143.164 |
| 825 | 74.048 | 144.879 | 25.475 | 145 |
| 850 | 75.249 | 147.107 | 21.825 | 146.866 |
| 875 | 76.404 | 149.305 | 18.12 | 148.762 |
| 900 | 77.516 | 151.473 | 14.36 | 150.686 |
| 925 | 78.586 | 153.612 | 10.546 | 152.637 |
| 950 | 79.616 | 155.721 | 6.68 | 154.615 |
| 975 | 80.609 | 157.802 | 2.76 | 156.618 |
| 1000 | 81.565 | 159.855 | -1.21 | 158.645 |
Table (3): The thermodynamics properties of blend.

| T(K) | Cp     | S       | ϕ      | H(T)-H(O) |
|------|--------|---------|--------|-----------|
|      | (J.mol⁻¹.K⁻¹) | (J.mol⁻¹.K⁻¹) | (J.mol⁻¹.K⁻¹) | (kJ.mol⁻¹) |
| 25   | 11.868 | 59.944  | 241.754 | 243.253   |
| 50   | 18.904 | 70.274  | 240.122 | 243.636   |
| 75   | 26.001 | 79.297  | 238.251 | 244.198   |
| 100  | 32.487 | 87.681  | 236.162 | 244.931   |
| 125  | 38.386 | 95.574  | 233.871 | 245.817   |
| 150  | 43.891 | 103.063 | 231.387 | 246.847   |
| 175  | 49.223 | 110.23  | 228.72  | 248.011   |
| 200  | 54.564 | 117.151 | 225.878 | 249.308   |
| 225  | 60.025 | 123.891 | 222.864 | 250.74    |
| 250  | 65.648 | 130.505 | 219.684 | 252.31    |
| 275  | 71.422 | 137.032 | 216.34  | 254.023   |
| 298.15 | 76.863 | 143.021 | 213.098 | 255.74    |
| 300  | 77.301 | 143.498 | 212.833 | 255.882   |
| 325  | 83.221 | 149.919 | 209.165 | 257.889   |
| 350  | 89.119 | 156.302 | 205.337 | 260.043   |
| 375  | 94.934 | 162.65  | 201.35  | 262.344   |
| 400  | 100.618 | 168.959 | 197.205 | 264.789   |
| 425  | 106.135 | 175.225 | 192.903 | 267.374   |
| 450  | 111.46 | 181.444 | 188.444 | 270.094   |
| 475  | 116.577 | 187.608 | 183.831 | 272.945   |
| 500  | 121.479 | 193.713 | 179.064 | 275.921   |
| 525  | 126.167 | 199.755 | 174.146 | 279.017   |
| 550  | 130.643 | 205.728 | 169.077 | 282.228   |
| 575  | 134.914 | 211.63  | 163.86  | 285.547   |
| 600  | 138.99 | 217.459 | 158.496 | 288.972   |
| 625  | 142.881 | 223.212 | 152.988 | 292.495   |
| 650  | 146.595 | 228.889 | 147.336 | 296.114   |
| Value | Column 1   | Column 2   | Column 3   | Column 4   |
|-------|------------|------------|------------|------------|
| 675   | 150.144    | 234.489    | 141.544    | 299.824    |
| 700   | 153.536    | 240.011    | 135.613    | 303.62     |
| 725   | 156.783    | 245.456    | 129.544    | 307.499    |
| 750   | 159.891    | 250.824    | 123.34     | 311.458    |
| 775   | 162.87     | 256.115    | 117.004    | 315.493    |
| 800   | 165.726    | 261.332    | 110.535    | 319.601    |
| 825   | 168.467    | 266.473    | 103.938    | 323.778    |
| 850   | 171.098    | 271.542    | 97.212     | 328.023    |
| 875   | 173.627    | 276.538    | 90.361     | 332.332    |
| 900   | 176.057    | 281.464    | 83.386     | 336.704    |
| 925   | 178.394    | 286.32     | 76.289     | 341.134    |
| 950   | 180.642    | 291.107    | 69.071     | 345.622    |
| 975   | 182.805    | 295.828    | 61.734     | 350.166    |
| 1000  | 184.888    | 300.482    | 54.28      | 354.762    |
Figure (2) reveals the relation between temperature and entropy of chitosan, PCL, and their blend in the temperature range 25-1000 K. Such a range of temperature cannot be reachable or obtainable in any experimental device.

![Figure (2) temperature versus entropy of the studied samples](image)

It was noticed from this figure that Chitosan has the largest entropy while the PCL has the lowest and the blend have intermediate values between both partners. The entropy for all of them increased by increasing the temperature in the range from 25-1000 K. It is evident that mixing Chi and PCL, the configuration of both of them changed to a new configuration.

Figure (3) shows the relation between both temperature and calculated specific heat capacity of the studied materials. It was observed that the heat capacity of studied polymeric materials was gradually increased in the temperature range from 25-1000 K, the rate of increase was found to be different for each partner. It is noted that Chi has the highest rate of increase over PCL while the blend shows an intermediate value between both polymers in full temperature range indicating some type of interaction and complexation between both Chi and PCL.

![Figure (3) temperature versus heat capacity of the studied samples](image)

Figure (4) shows the relation between temperature and free energy of studied samples. The free energies decreases with increasing temperature for all studied samples and the most probable reason for this behavior may be attributed to mixing effect.
Figure (4) temperature versus free energy of the studied samples

Figure (5) represent the relation between the temperature and the enthalpy of studied samples.
Energy optimization of the selected samples shows a three dimensional arrangement of the constituting atoms per unit cell which results in absorption behavior correlated to the frequency previously studied [12, 13] and compared and supported with published data of similar system [14, 15]. Such compatibility open gate for the comparison of other related data which can be obtained by the same route including thermodynamic parameters such as specific heat, entropy, free energy and enthalpy even in a non-reachable temperatures. Obtained thermodynamic parameters shows some type of interaction and complexation indicated by the intermediate values for semi-natural blend of all parameters over the whole studied temperatures (25-1000 K) with a comparable values at marked room temperature (289.15 K) in all graphs and tables. In addition, the absence of negative or imaginary frequencies in calculated data point out and support the structural arrangement of both virgin polymers and also in their suggested complexes poly blend. In the contrary of figures (2, 3 and 4) which show convex behavior according to equation (2), the enthalpy shows a concave behavior eq. (1).

Conclusions

Calculated vibrational spectra proved the equilibrium of suggested structures especially in the absence of imaginary frequencies. Present study indicates that the use of DFT can predict the thermodynamic parameters at temperatures not reached through any experimental methods. Obtained data of polymer blend lay between that of both polymeric constituents indicating interaction and complexation of polymer blend at all temperatures. The plot of the entropy and heat capacity as a function of temperature show a convex behavior while the enthalpy show a concave behavior supported by the given equations.

Conflicts of Interest

No conflict of interest.

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