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STATISTICAL THERMODYNAMICS OF LINEAR MACROMOLECULAR STRUCTURES: A SYSTEMATIC EXPANSION TO SIMHA-SOMCYNSKY LATTICE HOLE THEORY

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Abstract

The first models used in Statistical Thermodynamics of Linear Macromolecular Structures are mean field theories, which do not contain structural dependence. Simha-Somcynsky (SS), a Mean Field Theory where the measure of the disorder is stated as holes, has been used successfully in linear structures. The use of this theory in structures where the branched has started is of great importance in terms of the theoretical and practical studies. This study makes use of Lattice-Cluster Theory in order to adapt the theory to branched structures.

LİNEER MAKROMOLEKÜLER YAPILARIN İSTATİSTİKSEL TERMODİNAMİĞİ: SIMHA-SOMCYNSKY ÖRGÜ-BOŞLUK TEORİSİNE SİSTEMATİK BİR SERİ AÇILIMI

Özetçe

Lineer ların istatistiksel termodinamiğinde kullanılan ilk modeller, yapı bağımlılığı içermeyen ortalama alan teorileridir. (mean field theories) Bir ortalama alan teorisi olan ve örgüdeki düzensizliğin ölçüsünün boşluklarla(hole) ifade edildiği Simha-Somcynsky (SS) teorisi, lineer yapılarda başarıyla kullanılmaktadır. Bu teori dallanmanın başladığı yapılarda da kullanılması, teorik ve uygulamalı çalışmalar açısından önemlidir. Bu amaçla teorinin dallanmış yapılara adapte edilmesi için, zincir yapılardan hareket edilerek Örgü-Küme Teorisinden (Lattice-Cluster Theory) yararlanılacaktır.

Keywords: Macromolecule, Statistical Thermodynamics, Simha-Somcynsky Theory, Lattice-Cluster Theory.
Anahtar Kelimeler: Makromolekül, istatistiksel termodinamik, Simha-Somcynsky (SS) teorisi, Örgü-Küme Teorisi.

1. INTRODUCTION

In 1920, the German chemist Hermann Staudinger found out that the natural rubber, whose structures could not fully be explained, was actually a big molecular structure composed of small monomer units. This study, making it possible to comprehend the macromolecular structures and thus opening a new era, brought the Nobel Prize to Hermann Staudinger in 1953. These structures, having been synthesized in different traits, were subsequently used in many fields of our daily lives as an effect-raising and carrying agent in medicine and perfumery, stretch film in sensory materials, a good adhesive and isolation material and soft elastic solids in construction and manufacturing industries. [1] Due to having a wide range of uses, studies on the statistical thermodynamics of the macromolecular structures in order to determine their mechanical features immediately followed, generally focusing on chain polymers, which can analytically be modeled independently from the structure of the macromolecule.

Lennard-Jones and Devonshire (LJD) model, one of the first developed models, is also known as cell model, according to which the molecule is accepted to be moving in its potential hole made up by its neighbors as if in a cell. [2, 3] Prigogine, expanding the LJD theory to *s*-mer systems, assumed that the molecule or the segment is in motion and interaction with neighboring molecules determined by its interaction potential. SS later defined the holes in the lattice-like structure, and determined the statistical behavior by finding out the combination of the holes formed within the lattice and intermolecular site with the molecules. [6] This theory made use of the Flory-Huggins mean field theory, the first significant theory designed for chain structures. [7-9]

The first theories based on mean field theory and independent from the design of macromolecular structures failed in the statistical thermodynamics of branched macromolecules. Studies on branched structures served as attempts to mathematically correct the mean field theories. One of the most important of these studies is Lattice-Cluster Theory (LCT), developed by Freed et al. [10]

In this article, the SS theory used successfully in the statistical thermodynamics of chain structures, is adapted to branched structures. In SS theory, which is independent from the macromolecular architecture, the possible figure showing the settlement of macromolecule on the lattice is combinatory factor, an entropic statement. The terms that depend upon the structure of the macromolecule obtained through LCT are added to its combinatory factor as entropic contribution.

2. THEORIES

2.1. Simha-Somcynsky Lattice-Hole Theory and Structure-Dependent Entropic Contributions

According to the SS theory [6], lattice sites are occupied by polymer molecule and holes. The most important contribution to the partition function, which is used in determination of the statistical thermodynamic features of the polymer, comes from the entropic term combinatorial factor. The combinatorial factor is stated as polymer molecules and holes representing disorder in the polymer. The ratio of the occupied sites on all of lattice sites is y, which is called the volume fraction.

$$y = \frac{sN}{sN + N_b} \quad (1)$$

The configurational partition function is represented with the combinatorial factor, free volume and partition function.

$$Z_{conf} = g(N, y)\left[\upsilon_f\left(\tilde{V}, y\right)\right]^{cN} \exp\left[-\frac{E_0\left(\tilde{V}, \tilde{T}, y\right)}{kT}\right] \quad (2)$$

The combinatorial factor, which is represented with $g(N, y)$ and is the expression of occupation possibilities of the polymer molecules into the lattice sites, is obtained using the number of molecules, occupied site fraction and hole fraction.

$$g(N, y) = y^{-N}(1-y)^{-sN(\frac{1-y}{y})} \quad (3)$$

This factor in the SS theory is derived from Flory-Huggins Mean Field Theory. If structure-dependent terms are added to this factor, which is valid for chain structures, the SS theory can also be used for branched structures.

The structure-dependent terms to be added to the combinatorial factor as correction terms include interactions of interchains and intrachains. These interactions will be obtained through bond vectors and added to the Mean Field Theory. Bond vectors interactions are obtained under the condition that **q** bond vector is not equal to 0 ($\mathbf{q} \neq 0$). The correction resulting from the architecture of the structure and applied on the Mean Field Theory is represented as follows:

$$Z = Z^{MF}\left(1+\sum_{D,B}\gamma_D D_B\right) \qquad (4)$$

The total symbol here is the correction term made up of the lattice-dependent term (D_B) and the term dependent on polymer architecture (γ_D), and obtained with diagrams. Obtaining the correction terms is algebraically difficult. Simpler and more standardized diagrams are used in order to represent algebraic operations. The diagrams obtained are classified, beginning with 1-bond, according to the number of bonds (1-bond joins two monomers). All diagrams are identified up to a certain number of bonds and the values of these diagrams are found. The total number of all the diagram values is expanded. Finally the mean field terms and the additional correction terms are obtained as follows: [11]

$$\frac{\Delta s}{N} = \Delta s^{mf,ss} - sa_0(1-y) - sa_1 y(1-y) - sa_2 y^2(1-y) \quad (5)$$

a_0, a_1, a_2 coefficients are identified, as a result of the series expansion, depending on the polymer architecture. [12]

$$
\begin{aligned}
a_2 &= \frac{2S_1^{\,4}}{s^4}\frac{1}{z^2} \\
a_1 &= \frac{2S_1^{\,4}}{s^4}\frac{1}{z^2} + \frac{8S_1^{\,3}/3 - 2S_1^{\,4} + 2S_1^{\,2}S_{11}}{s^3}\frac{1}{z^2} \\
a_1 &= a_2 + \frac{8S_1^{\,3} - 2S_1^{\,4} + 2S_1^{\,2}S_{11}}{s^3}\frac{1}{z^2} \\
a_0 &= a_1 + \frac{2S_1^{\,2}S_2 + S_2^{\,2} + S_1(-2S_{12} - 4S_2 - 2S_3 - 6S_d)}{s^2}\frac{1}{z^2} + \frac{S_1^{\,2}}{s^2}\frac{1}{z} \\
A &= a_0 + \left(-\frac{S_2^{\,2}}{2} + \frac{S_{22}}{2} + S_3 + 2S_d + S_{du} + S_{duu} + 3S_p \right)\frac{1}{z^2} - \frac{S_2}{s}\frac{1}{z}
\end{aligned}
\tag{6}
$$

S-terms represents for bond interactions and must be calculated according to the polymer being applied.

2.2. Acquisition of Polyethylene (PE) and Polypropylene (PP) Structures and Structure-dependent Contributions

The most fundamental structure whereby the structure coefficients in the correction terms can be acquired easily and the theory can be tested is PE, a linear chain structure. PE is a molecule constituted by *n*- ethylene molecules in the shape of a chain.

$$\ldots - CH_2 - CH_2 - CH_2 - CH_2 - \ldots \qquad (7)$$

If CH_2 is considered as a segment, PE chain structure is shown as follows:

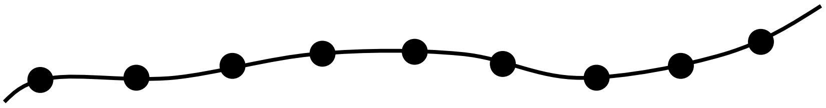
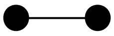
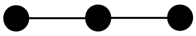
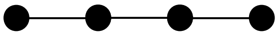
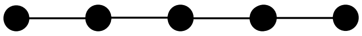
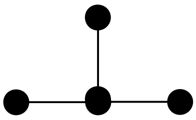
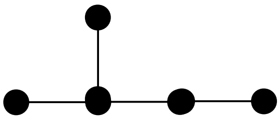
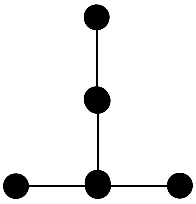


Figure 1. The segmental demonstration of the PE chain structure

Each segment in the shape represents for the ethylene. In the calculation of the coefficients depending on the polymer structure, settlement of a bond on the molecule and its interaction with the other bonds were counted.

Table-1 The Coefficients Dependent on the PE Structure

S_n	**Shape of Bond**	**The Counting in terms of bond number**
S_1		*N*
S_2		*N-1*
		*N-2*
S_4	S_3 	*N-3*
S_d		*0*
S_{du}		*0*
S_{duu}		*0*

Thus, the structure-dependent coefficients for PE are acquired as bond numbers. Coefficients to be obtained depending upon branching could not be found. The other coefficients were identified sequentially in a simple way.

The unit structure of PP is propylene and its bond structure is as shown below. PP is a molecule constituted by *n*-propylene molecules.

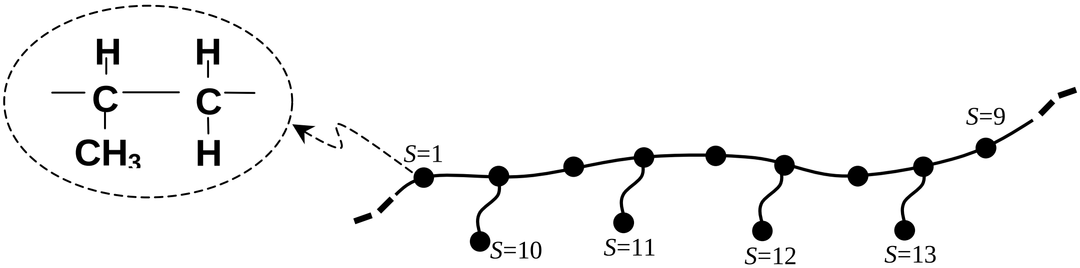
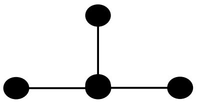
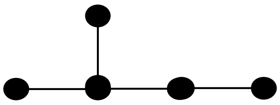
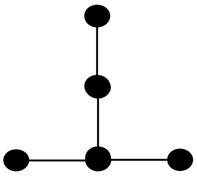


Figure 2. The Segmental Demonstration of the PP Structure

The PP segmental structure has a branch on the backbone. PP is also accepted the basic branched structure.

Table-2 The Coefficients Dependent on the PP Structure

S_n	**Shape of Bond**	**The Counting in terms of bond number**
S_1	●—●	*3N/2*
S_2	●—●—●	*2N-1*
	●—●—●—●	*2N-4*
S_4	●—●—●—●—●	*2N-5*
S_d		$N/2$
S_{du}		*N-2*
S_{duu}		*0*

For PP, considered to have one branch, the structure-dependent coefficients were acquired as bond numbers. The bond interactions, previously representing branched in PE, were found to be zero.

3. APPLICATIONS ON POLYETHYLENE (PE) VE POLYPROPYLENE (PP) STRUCTURES

For the PE linear polymer structure and the PP, considered to have one branch, isobar graphs in the specific volume-temperature change were obtained and, using experimental methods, the results of the theory including the correction terms were compared.

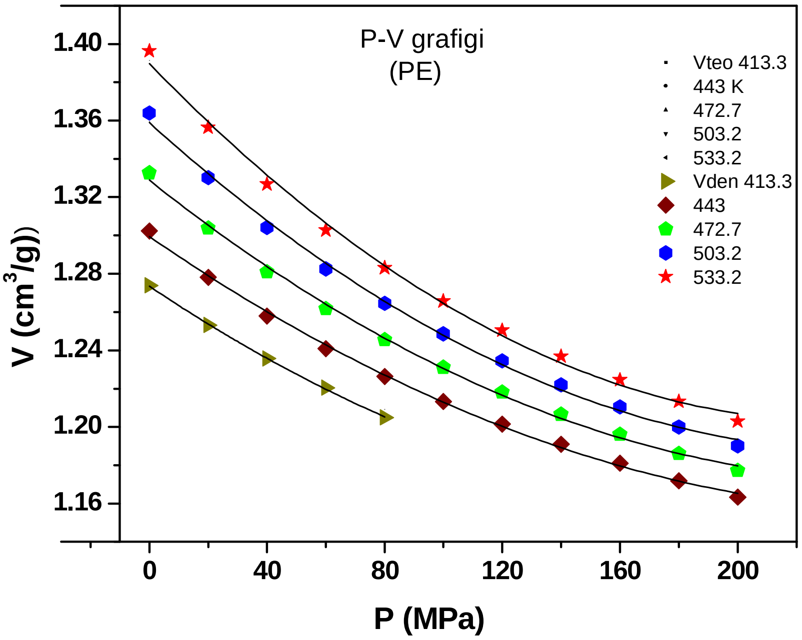


Figure 3. The Specific Volume-Pressure Change of the Experimental and Theoretical Values for the PE (isothermal)

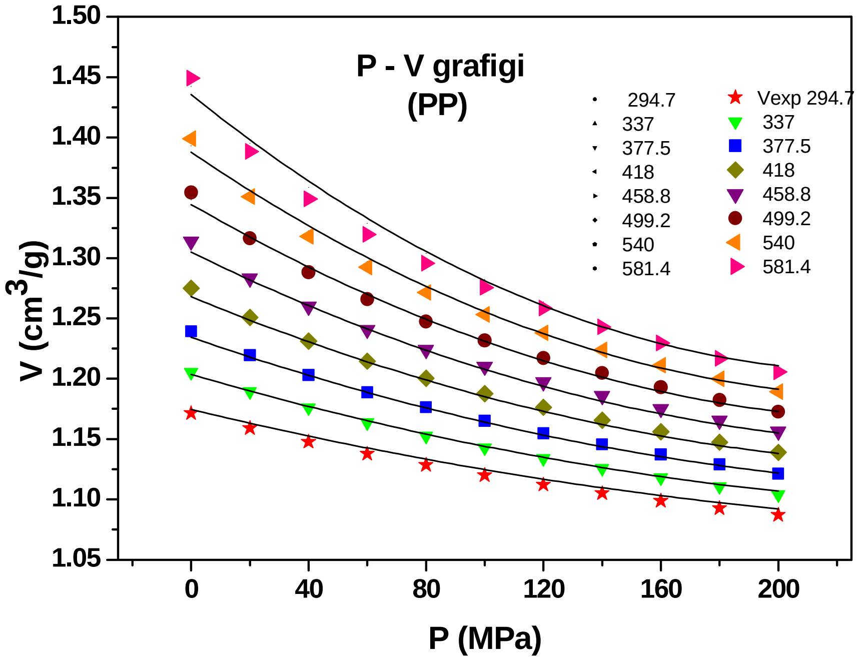


Figure 4. The Specific Volume-Pressure Change of the Experimental and Theoretical Values for the PP (isothermal)

The theoretical and experimental data for both the PE and PP structures were found to be compatible. However, there were trivial mistakes (~ %1) in the low pressure and high temperature zone.

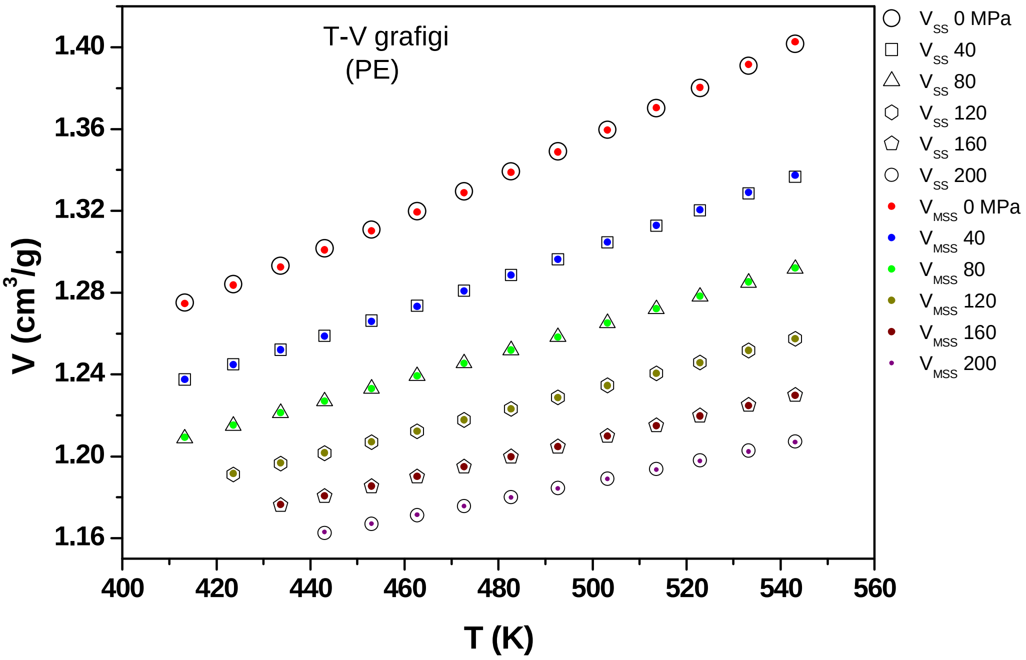


Figure 5. The Comparison of specific volume-temperature changes of the SS theory and the theory including the correction terms for the PE structure (isobar)

The results of the SS theory were compared with the SS theory including the correction terms. The findings show a similar change in the pressure and temperature zone.

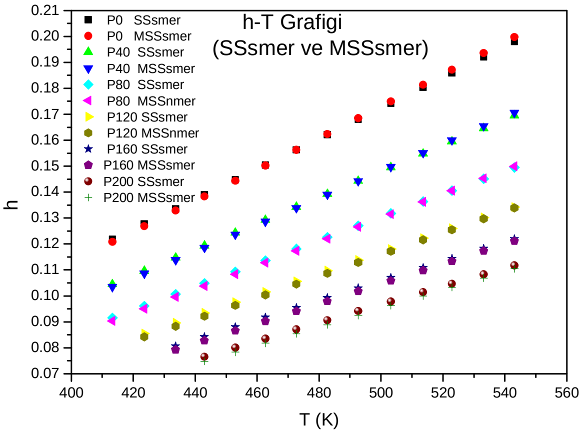


Figure 6. The Comparison of the hole fraction-temperature change with the SS theory and the theory including the correction terms fro the PE (isobar)

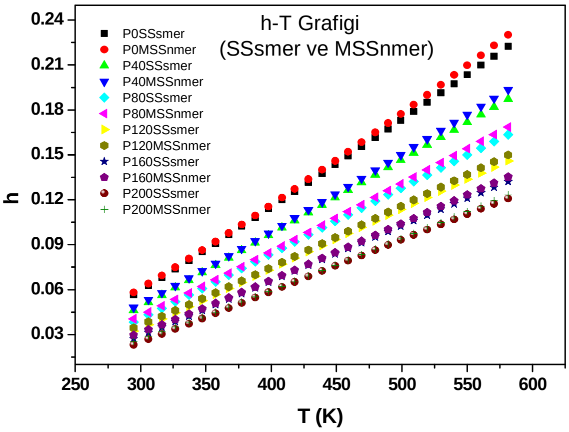


Figure 7. The Comparison of the hole fraction-temperature change with the SS theory and the theory including the correction terms fro the PP

Determining the hole fraction, which is crucial in terms of the experimental studies done on the polymer structures, is very important. The hole fraction for PE and PP structures were theoretically determined for the separate temperature and pressure zones. The theory and the corrected theory brought about similar outcomes, except for low pressure and high temperature zones.

4. CONCLUSION:

The contributions belonging to macromolecular structure were added to the SS theory, used in the statistical thermodynamics of linear structures. The lattice-dependent terms and the contribution terms consisting of the terms dependent on the molecule structure were obtained through diagrams instead of long algebraic operations.

Several implementations were carried out on the PE of the linear structure and the PP where the branching partially started. The isobar curves for the specific volume-temperature change and the hole fraction-temperature change were obtained. The SS theory and the corrected SS theory were compared through these implementations, bearing similar findings. The fact that the corrected theory worked out indicated its applicability.

Structure-dependent coefficients required for the corrected theory were calculated for the PP structure having one branch. Further studies can be carried out by determining these coefficients for other structures having similar branched. Thus, the SS theory used in linear structures can also be used together with the correction terms for other branching structures.

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