Studying The Characteristic Parameters and External Freedom Degree of Polyethylene in different Molecular Weights By Hole Theory

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ABSTRACT

$\mathbf{T}$he external degree of freedom of linear and branched molecules of polymers played an important role in new polymer synthesis. The theory Simha-Somcynsky (SS) which established for the first time the statistical thermodynamics and polymers state of equation, using the mean field theory (that does not depend on the structural of materials). Expressed through the zeroth-order mean field theory through the hole vaccume cells as a measure of irregularity in the lattice. The (SS) theory has achieved quantitative success in statistical thermodynamics of polymers. The SS theory has been applied to extract the external degrees of freedom for polyethylene at different molecular weights. The external degree of freedom is very important parameter to specify the thermodynaics characteristic parameters. Applying SS hole theory, the thermodynamic properties of polyethylene was studied for temperature from 353K up to 473 and pressure from o.1Mpa up to150 Mpa. The minimum and maximum deviations in specific volume was found to be 0.045 (PE2100) and 1.138 (PE156) respectively..

Introduction
Simha-Somcynsky (SS) Hole Theory:
Simha-Somcynsky (SS) developed an equation of state (EOS) based on the lattice-hole model[1] introducing the temperature and volume dependent occupied site fraction, $y(V,T)$. The Simha and Utraki [2] has differentiated from cell theories[3], the state an equation obtained is applied to low molecular weights [4], macromolecules and mixtures [5-6] and quantitative success has been achieved. Expressed with polymer filled and hole theory[7]. The occupied site fraction, $y(V,T)$, and the complementary hole fraction $h(V,T)$, are given by the following equation:
$$y = 1 - h = \frac{Ns}{N_h + Ns} \quad ...(1)$$

where N and N_h are the number of molecules and holes respectively and s is the number of segments in a molecule. The configuration partition function [8], Z_{conf} for N polymer molecules consisting of s segments and the proportion of occupied and empty cells, is given as in below.

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

Where $g(N,y)$ the combinatorial factor by Poser and Sanches[9]., that is the total number of distinguishable degenerate arrangements of the holes and molecules is expressed as

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

The free volume υ_f by Carri and Simha[10]. expressing the amount of void in the lattice is given as in below;

$$\upsilon_f = \upsilon^*\left\{y\left[\left(y\tilde{V}\right)^{1/3} - 2^{-1/6}\right] + (1-y)\left(y\tilde{V}\right)^{1/3}\right\}^3 \quad ....(4)$$

Here, the first part of the free volume an equation represent voids in filled cells, (free volume fraction) intracellular spaces, and the second part is the spaces in the lattice sites, that is represent empty cells.
The total lattice energy E_0 for s-mer is *given by*;

$$E_0 = \frac{1}{2} yNq_z\varepsilon^*\left[A\left(\frac{\upsilon^*}{\omega}\right)^4 - 2B\left(\frac{\upsilon^*}{\omega}\right)^2\right] \quad ...(5)$$

Here $\omega = yV/sN$ is amount of occupancy. ε^* is the characteristic lattice energy of system in equilibrium state and q_z the number of contacts between pairs nearest adjacent segments.

$q_z = s(z-2) + 2$ ....(6)

The total external degree of freedom $(3c)$ that determines the flexiblity for an ideal chain as given by; $3c = s+3$ .... (7)

By substituting all above equations in configuration partition function then substitutes in configurable free energy equation F_{conf} we get configurable free energy of the system.

$F_{conf} = -kT \ln Z_{conf}$

$$= NkT \ln y + kTsN\left(\frac{1-y}{y}\right)\ln(1-y) \qquad ....(8)$$

$$-3kTcN\left\{\ln\left[\left(y\tilde{V}\right)^{1/3} - 2^{-1/6}y\right] + \frac{1}{3}\ln\left(v^*\right)\right\}$$

$$+\frac{1}{2}yNq_z\varepsilon^*\left(y\tilde{V}\right)^{-2}\left[1.011\left(y\tilde{V}\right)^{-2} - 2.409\right]$$

is obtained as. In the case of balance, the occupancy rate of the system does not change; In this case, the derivative of the system free energy should be equal to zero according to the occupancy rate:

$$\left(\frac{\partial F}{\partial y}\right)_{\tilde{V},\tilde{T},c/s} = 0 \;\cdots\cdots \;(9)$$

$$\frac{s}{3c}\left[\frac{s-1}{s} + \frac{\ln(1-y)}{y}\right] - \frac{\eta - \frac{1}{3}}{1-\eta} - \frac{y}{6\tilde{T}}\left(y\tilde{V}\right)^{-2}\left[2.409 - 3.033\left(y\tilde{V}\right)^{-2}\right] = 0$$
...(10)

$\eta = 2^{-1/6}y\left(y\tilde{V}\right)^{-1/3}$ the derivative of free energy by volume gives the expression of pressure.

$$P = -\left(\frac{\partial F}{\partial V}\right)_T = P\left[\tilde{V},\tilde{T}\right] = P\left[\tilde{V},\tilde{T};y\left(\tilde{V},\tilde{v}\right)\right] \;....(11)$$

Thus, the state equation to be used in polymers is obtained.

$$\frac{\tilde{P}\tilde{V}}{\tilde{T}} = \frac{1}{1-\eta} + \frac{2y}{\tilde{T}}\left(y\tilde{v}\right)^{-2}\left[1.011\left(y\tilde{v}\right)^{-2} - 1.2045\right] \;\cdots (12)$$

Explicit expression of reduced parameters that establish the link between theoretical values and experimental values is.

$$\tilde{P} = \frac{P}{P^*}, \qquad \tilde{V} = \frac{V}{V^*}, \qquad \tilde{T} = \frac{T}{T^*} \;...(13)$$

The characteristic reducing parameters that establish the relationship between theoretical and experimental parameters are given below.

$$P^* = \frac{cT^*R}{mV^*}, \qquad V^* = \frac{\upsilon^*s}{m}, \qquad T^* = \frac{q_z\varepsilon^*}{c} \;...(14)$$

It is expressed. Then the charateristic parameters relalation equation as in below.

$$\left(\frac{P^*V^*}{T^*}\right)M_o = \left(\frac{c}{s}\right)R \quad ...(15)$$

M_o is the mass of the unit segment of the molecule and R gas constant.

The Lennard-Jones-Devonshire, Prigogine cell model and fluid phase [12-16], and these cell models, a modified with the hexagonal package structure was developed by Dee and Walsh [17]. In order to obtain the average interaction parameter and repulsive volume characteristics from these parameters. These parameters are separated into different molecular units that may be on the lattice. For this, the necessary decomposition equations are solved and interaction energy ε^* and repulsive volume υ^* parameters are obtained.

The average error and maximum error in the specific volume, are given as in below.

$$\Delta V_{average} = \frac{100}{N}\frac{\left|V_{ith} - V_{iexp}\right|}{V_{iexp}} \;...(16)$$

$$\Delta V_{max} = \max(\Delta V_i)$$

The Results and Discussion

Table 1 shows the characteristic parameters of polyethylene at different molecular weights

Polymers	$s = n$	c	P^*(Mpa)	V^* (cc/g)	T^*(K)	$10^6\upsilon^*$(cc/g)	ε^*(K)
PE156	11	1.7	728.1	1.245	10028	17.74	152.2
PE226	16	1.8	689.3	1.237	12903	17.70	148.2
PE338	24	1.9	657.7	1.229	17865	17.51	143.4
PE1100	78	4.7	678.7	1.214	23434	17.30	140.8
PE2100	150	10.8	692.2	1.201	24617	16.92	139.2

By applied the SS theory have been extracted some of important thermodynamic parameters as in table1, external degree of freedom, characteristic PVT, repulsive volume between segments and characteristic energy parameters, obtaining the values of a parameters is the purpose of this study.

Table 2 shows the characteristic values and the minimum and maximum deviations in volume at different molecular weights of polyethylene

Polymers	$\left(\frac{P'V^*}{T^*}\right)\times10^{-3}$	$(R/M_o)x10^{-3}$	%Min. Err	%.Max. Err
PE156	90.4	53.2	0.418	1.138
PE226	66.0	36.7	0.212	0.914
PE338	46.2	24.6	0.104	0.766
PE1100	35.6	7.5	0.059	0.240
PE2100	33.8	3.9	0.045	0.130

The values of charateristic parameters for different molecular weights of polyethylene are calculted intable2 to extract the chains of polyethylene is flexible or not as showed in graph6 .

Table 3 shows the hole fraction $(h = 1 - y)$ values of polyethylene

| Temp.(C)	PE156	PE226	PE338)	PE1100	PE2100
80	0.174	0.143	0.109	0.088	0.082
100	0.193	0.159	0.123	0.010	0.093
120	0.212	0.176	0.137	0.112	0.105
140	0.231	0.193	0.151	0.125	0.117
160	0.251	0.214	0.166	0.135	0.130
180	0.272	0.228	0.181	0.150	0.143
200	0.293	0.246	0.196	0.163	0.156
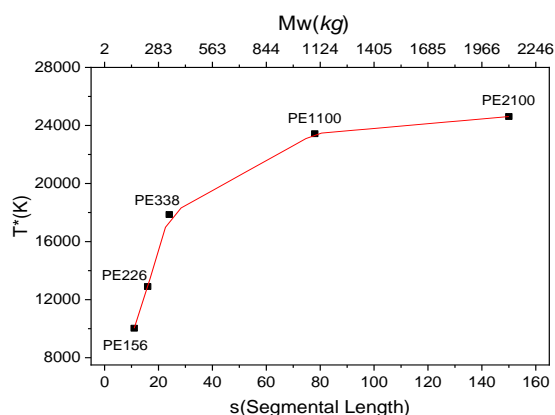
Fig. 1: The values T* for different molecular weights of polyetylene as a function of segmental length.

The figure 1 shows that the characteristic temperature of the polymer chain is highly dependent on the number of segments, in this study we have identified the characteristic temperatures increasing as the segment lentgh increases, the main reason belong to the number of contact pairs of segment increases and identified the segment length more 150, characteristic temperature remains constant.
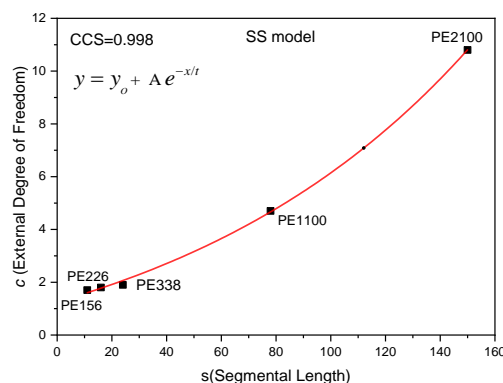

Fig. 2: showing the degree of external freedom with segment lentgh

This graph shows that as the segment length increases, the degree of external freedom has been found to increase logarithmically. The most important thing that focuses us on this study is to determine the value of external degree of freedom and to learn about its behavior.
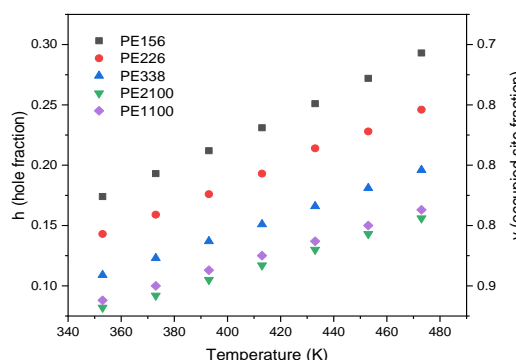
Fig. 3: The values hole and occupied site fractios for different molecular weights of polyetylene.

The data of this graph have been extracted by using the SS theorey their themodynamic properties especially the hole fraction in the range of 353-473 K temperatures as in table3. Shows the relationship of different molecular weights to the temperature equivalent .There are two important determinations in this graph, the first is shown less hole fraction as the molecular weightincreases, the second identified the temperature increases leads to increase in hole fraction.
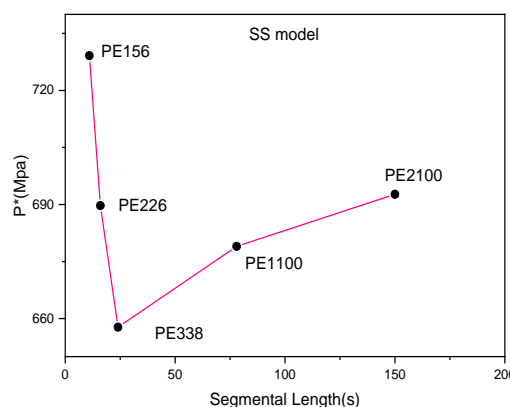
Fig. 4: The values P* for different molecular weights of polyetylene as a function of segmental length.

The characteristic presure of low molecular weight in polyethylene (PE156) İ it is an expected value that will have high, characteristic pressure has decreased when molecular weight increased, but for macromolecularstructures (PE1100, PE2100) the characteristic pressure increase as the molecular weight increases, because cross-links are more in macromolecular structures**.**
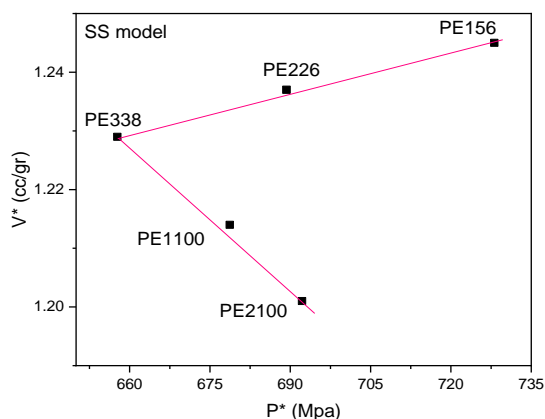

Fig. 5: Shows the relation between the characteristic V* versus the characteristic pressure P* .

This graphic shows two independent equations.The first event characteristic volume and characteristic pressure decrease when increasing molecular weights (PE156, PE226 and PE338), the second event when molecular weghts increases (PE338, PE1100 and PE2100) leads to decreases in characteristic volume and relative increases in characteristic pressure, the reason for thisis that as the molecular weight increases the cross-links increases.
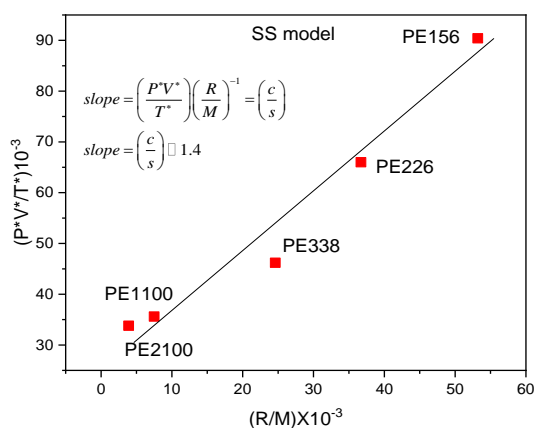

Fig. 6: Shows the relation between the characteristic parameters versus the inverse of molecular weights

The figure6 give for us the important information properties about chains behavior the characteristic parameters (P*, V* and T*) from the table2, with the inverse of the molecular weight. It gives us information about the structure of the chain molecule, it is found that the slope is proportion between externel degree of freedom to number of segment and found the value of this proportion around one and a half, this mean the polyethylene acts as if the average chain molecule acts as a rod and acts with less order of freedom than a monomer, obtaining this information is one of the aim of this study, because this information will help us synthesize new polymers.

İn this study, Newton Raphson Method is used as one of the impotant tools, NRM methodis used in the solution of equations 10 and 12 nonlinear equations and an iteration is needed to start for most appropriate external degree of freedom solution by chracteristic parameter correlation (equa.15). İterasion is made up to the most appropriate value under the conditions. On the other hand the matrix is used to solve the state of equations for reduced temperature and reduced volume formed as a result of iteration. Since the matrix isnot a diagonal matrix, the Pseudo İnverse Matrix Technique (PİMT) were used so that the most appropriate parameter values were found forsolved equations.

Conclusions

This study has reached very good results that can be decided in accordance with its purpose,

One of the most important results was determinedthat the external degree of freedom varies according to the weight of the polyethylene molecole. It has been lagarithmically elevated in macromolecular structure and the ratio of the external degree of freedom to the segment length indicates that there is relative flexibility in the chain structure of polyethlene for differet molecular weight s have been studied. Other parameters were to be compatible with the expermental especially the hole fraction and specific volume depends on temperature. As it is known, the polymertypes are few in nature, the industry world prefer polymer synthsis. The aim of this study is the ability of polyethylene to be synthesized. Finally, according to the results have been obtained by using the SS theory as in three tables, new polymers could be obtained for the polymerization process and brought to the world industry.

References

[1] Simha, R. Somcynsky, T., (1969) On Statistical Thermodynamics of Spherical and Chain Molecule Fluids. Macromolecules, **2**(**4**), 342.

[2] Utracki, L.A. Simha, R. (2001) Analytical representation of solutions to lattice-hole theory. Macromolecular Theory and Simulations, **10**(**1**), 17-24.

[3] Buta, D; Freed, K.F.: (2002). "Lattice polymers with structured monomers: A Monte Carlo study of thermodynamic properties of melts and solutions", *J. Chem. Phys*, **116**(**24**) p:59-66 .

[4] Simha, R. Yahsi, U., (1995) Statistical Thermodynamics of Hydrocarbon Fluids - Scaling Parameters and Their Group Contributions. Journal of the Chemical Society-Faraday Transactions, **9**1(**16**), 2443-2455.

[5] Rodgers, P.A., (1993) Pressure Volume Temperature Relationships for Polymeric Liquids - a

Review of Equations of State and Their Characteristic Parameters for Polymers. Journal of Applied Polymer Science, **48**(**6**),P:1061-1080.

[6] Zoller, P., (1990) Polymer Handbook. Brandrup, J., Immergut, E.H.; Wiley Interscience, USA, New York, 110-120.

[7] Jain, R.K. Simha, R., (1980) On the Statistical Thermodynamics of Multicomponent Fluids - Equation of State. Macromolecules,. 13(6), 1501-1508.

[8] Sperling, L.H., (2006) Introduction to Physical Polymer Science. John Wiley & Sons, Inc.,. Hoboken, New Jersey, USA.

[9] Poser C.I., and Sanchez I. C.;(1989). Colloid interface Sci. J. Chem. Phys 69: 1307-1312 .

[10] Carri G. A. and Simha R. J., (1996)Colloid Interface Sci.J. Phys. 178: 483-494 .

[11] Nuri S. M., (2017)." Extracting the density gradient profile of polyethylene glycol from Bulk to surface ", Journal of Kirkuk University; college of scıence **12**(**4**).

[12] Sedlacek, T., et al, (2005) On PVT and rheological measurements of polymer melts -

Correction of the hole fraction-viscosity relationship. International Polymer Processing, **20**(**3**), 286-295.

[13] Lennard-Jones, J.E., Devonshire A.F., (1937) Critical Phenomena in Gases. I. Royal Society of London. Series A, Mathematical and Physical Sciences., 163, 53-70.

[14] Lennard-Jones, J.E., Devonshire, A.F., (1938) Critical Phenomena in Gases. I., Royal Society of London. Series A, Mathematical and Physical Sciences, 165, 1-12.

[15] Aslan, M.,Ph.D. thesis. Yahsi, U.(2009). Dallanmış ve Dendrimer Makromoleküler Yapıların İstatistiki Termodinamiği i Doktora Tezi, Marmara Üniversitesi Fen Bilimleri Enstitüsü, İstanbul, Türkiye, P.17-27.

[16] Kahl, Heike, and Sabine Enders.,(2000) "Calculation of surface properties of pure fluids using density gradient theory and SAFT-EOS." *Fluid Phase Equilibria* **172**(. **1**): P.27-42.

[17] John Wiley & Sons, (**2006**), "Handbook of Introduction to Physical Polymer Science" Inc., Hoboken, New Jersey in Canada, L.H.S perling .-4th ed QD381.S635 USA , p: 58-129.

دراسة الخواص المميزة ودرجة الحرية الخارجية للبولي إيثيلين في الأوزان الجزيئية المختلفة باستخدام نظرية الجزءِ الفراغي

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الملخص

تلعب الدرجة الخارجية لحرية الجزيئات الخطية والمتفرعة من البوليمرات دورًا مهمًا في تخليق البوليمرات الجديدة. SimhaSomcynsky(SS) التي أسست للمرة الأولى الديناميكا الحرارية الإحصائية و معادلة حال لبوليمرات، والتي استخدمت نظرية المجال المتوسط التي لا تعتمد على هيكلية المواد. معبرًا عن نظرية مجال من المرتبة الصفري من خلال الخلايا الغير المملوء مقياس في الشبكية. حققت نظرية (SS) نجاحًا كميًا في الديناميكا الحرارية الإحصائية للبوليمرات. تم تطبيق نظرية SS لاستخراج الدرجات الخارجية من الحرية للبولي إيثيلين في الأوزان الجزيئية المختلفة. تعتبر درجة الحرية الخارجية من الخواص مهمة جدًا في تحديد المتغيرات المميزة للديناميكا الحرارية، من خلال تطبيق نظرية الفجوات ، تم الحصول على الخواص الديناميكية الحرارية للبولي إيثيلين ما بين درجة الحرارة K 473-353 والصغط ما بين 0.1-150 Mpa . وتم الحصول على الحد الأدنى والحد الأقصى في الانحراف الحجم النوعي 0.045 في(PE 2100) و 1,138 في (PE 156) على التوالي.