



## Extracting the Density Gradient Profile of Polyethylene Glycol from Bulk to Surface

S. M. NURI

College of Education For Pure Science Physics Dept./Kirkuk

<sup>1</sup>[Saygin.kuzeci@yahoo.com](mailto:Saygin.kuzeci@yahoo.com)

### ABSTRACT

*In this work the Simha and Somcynsky (SS) lattice hole theory in conjunction with Cahn-Hilliard(CH) model have been used, (SS) theory describes the thermodynamic properties of both low and high molecular weight in terms of hole fraction, On the other hand (CH) describes the free energy profile of polymer surfaces or interfaces as an inhomogeneous mixture. CH consider the energy density to be two fold. The first is the constant free energy density for a homogeneous region of the system and the second is the density gradient contribution to the free energy. Have employed the mentioned theories in derive the new equations to extract in surface tension and surface depth profile in terms of chemical potential by means of SS theory. Starting form the atmospheric pressure to 150Mpa and for temperature range from 313 to 473 K, Then it is found the density profile of polyethylene glycol decrease as it is approached to the surface. PVT characteristic parameters of the SS theory are calculated using the data of polyethylene glycol. the average and maximum value (at polyethylene glycol in different molecular weight) of percentage deviation of specific volume found to be 0.03 and 0.28 respectively.*

**Keywords:** *lattice hole theory, Chan-Hilliard, occupied site fraction,density profile , PEG, surface tension*



## حساب كثافة الشد السطحي لبولي اثيلين كلايكول من العمق الى السطح

### ملخص

( ونظرية CH نظرية الفجوات بالارتباط مع كاهن هيلياردSS في هذه الدراسة استخدمت نظرية سمهاسومينكي تضمن الجزئيات ذات الاوزان الجزئية الواطئة والعالية ، ومن ناحية اخرى يصف نظرية كاهن هيليارد SS) الطاقة الحرة في السطح البوليمرات أو الطاقة الحرة في الوصلة ما بين عمق والسطح في الجزء المتجانس كثافة الطاقة الناتجة عن مساهمة اولهما كثافة الطاقة المتجانسة CH والغير المتجانس في المادة ، يعتبر والثانيهما هي ميل الطاقة من المنطقة الغير المتجانسة الى الطاقة الحرة ، وقد استخدمنا النظريات المذكورة في اشتقاق المعادلات الجديدة ولأول مرة (بولي أثيلين كلايكول) للانتزاع في الشد السطحي ولمحة عن العمق 473K الى 313K ودرجة الحرارة من 150Mpa الكيمائي للبوليمر تحت الدراسة ابتداءً من الضغط الجوي الى وكانت نسبة الخطأ الحد الادنى والأقصى للحجم النوعي او الانحراف عن نسب الحقيقي لبوليمر بولي اثيلين على التوالي 0.28 و 0.03 كلايكول المستخرجة هي

الكلمات الدلالية : نظرية سمهاسومينكي ، نظرية كاهن هيليارد ، نسبة المواقع المحتملة ، لمحة كثافة ، الشد السطحي ، بولي اثيلين كلايكول .

### 1. Introduction

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[kirkukjournsci@gmail.com](mailto:kirkukjournsci@gmail.com)



Surface density profile and surface tension of polymers play an important role in polymer blending, wetting, coating, adhesion, foaming , comprehensive role in the description , understanding of many processes and enormous of industrial importance.

The theory is used by Cahn-Hilliard(CH), that includes the free energy profile of the system that consist of more than one phase .The total free energy of the liquid polymer system is formation by two kind of contribution, the first contribution is from homogeneous region and second contribution is from inhomogeneous region and  $\kappa$  is a positive materials constant called the gradient energy coefficient or interaction coefficient for the component is the composition gradient contribution to the free energy. The lattice fluid (LF) theory [1] is able to describe the thermodynamic properties of both low and high molecular weight. The LF model in conjunction with the Cahn-Hilliard theory (CH) is employed to develop a method for calculating the surface tension of nonpolar and slightly polar liquids of arbitrary molecular weight has worked by Poser and Sanchez[ 2] to extract the surface tension and surface density profile of polymers in broad range of temperature. Poser and Sanchez, Kahl and Enders [3 ] , Dee-Sauer and C.Miqueu and co-workers they has worked extensively on the surface tension and surface density profile of polymers for broad ranges of temperatures and molecular weights using the Cahn-Hillard density gradient[4].

Theory in conjunction with the Flory, Orwoll, and Vrij (FOV) [5] and Sanchez and Lacombe [6] (SL) equation of state theories. B. Sauer and T. Dee they has worked to obtained the surface tension and the gradient energy coefficient ( $\kappa$ ) for linear, branched *n*-alkanes . The surface tension increase and surface entropy decrease with increasing molecular weight .The results of this study of various molecular weight of polyethylene glycol confirms the correlation between molecular weight and surface entropy.

The surface thermodynamics properties of polymers are strongly correlated with the bulk properties, the bulk properties are inherently hole fraction dependent so we could constitute the correlate between surface tension and surface density profile



with hole fraction or free volume of the bulk, Carri and Simha (CS) [7 ] examined the relation between surface tension and hole fraction of the bulk properties by means of SS lattice-hole theory.

The Simha and Somsynsky (SS) come up with an arrangement in the model increasing the disorder by employed hole fractions in the underlying quasi lattice model. An established equation of state( E.O.S) was intensively applied to low and high molar mass of liquid polymers[8,9] and mix of molecular weight of different polymer[10], with significant quantitative achievement,

The quantitative success of hole theory (SS) encouraged us to employ in conjunction with the Cahn-Hilliard density gradient theory to inspection how the hole fraction changes from the bulk to surface and effectives on surface tension and its correlation with the surface density profile of binary polymers system. we are employed properties of SS theory as a nested with CH in the range of about 473 K temperature and up to about 1500 bar pressure. We have obtained %0.28 maximum deviation in volume. The aim of this study is how the density profile changes from bulk to surface or interface and interface thickness by using the mentioned theories.and our main reason from this study is investigation the parameters that play important role in innovation the new polymers..

## **2 . Theories**

### **2.1 The Cahn-Hilliard Theory**

The Cahn-Hilliard theory [11] correlates the thermodynamic characteristics of a system with an interface between two non-condensing phase. In the interface between the liquid and the gas phase of a pure polymer in equilibrium condition , the density of the composition discontinues or behaves as gradient. , consider a binary alloy in a two phase equilibrium state.



For the free energy of inhomogeneous systems the density gradients varies from the bulk or liquid density to the surface or the vapor density continuously. This means that the Helmholtz free energy density,  $\alpha$ , of a system with an interface can be obtained by expanding the Helmholtz free energy in Taylor series around the equilibrium state[11]:

$$\alpha(\rho, \nabla\rho, \nabla^2\rho, \dots) = \alpha_0(\rho) + \kappa_1 \nabla^2\rho + \kappa_2 (\nabla\rho)^2 + \dots \quad (1)$$

where  $\alpha_0(\rho)$  is the local free energy density of homogeneous polymer system and the coefficients of Laplacian and gradient density terms are

$$\kappa_1 = \left( \frac{\partial \alpha}{\partial \nabla^2 \rho} \right)_0; \quad \kappa_2 = \frac{1}{2} \left( \frac{\partial^2 \alpha}{\partial (\nabla \rho)^2} \right)_0. \quad (2)$$

The subscript 0 in Eq. (2) indicates that the derivatives are to be evaluated in the limit of  $\nabla\rho$  and  $\nabla^2\rho$  going to zero. Here the density variation is assumed comparatively small to the reciprocal of the intermolecular distance.

The Helmholtz free energy,  $A$ , of a system of volume  $V$  is given by

$$A = \int_V [\alpha_0(\rho) + \kappa (\nabla\rho)^2] dV \quad (3)$$

where  $\kappa$  is the gradient energy coefficient for the system. It is composed of two terms: the first is the local free energy of homogeneous system and the second is composition gradient contribution to the free energy.

We could write Eq. (3) in finally shape of surface tension for a planar interface tension is given

$$\sigma = \int_{-\infty}^{+\infty} [\Delta\alpha + \kappa \left( \frac{d\rho}{dx} \right)^2] dx \quad (4)$$

where  $\Delta\alpha = \alpha_0(\rho) - (\rho_l \mu_{l0} + \rho_v \mu_{v0})$  is the difference between the Helmholtz free



energy density of a homogeneous fluid of density  $\rho$  and two phase equilibrium mixtures with liquid and gas states.

where  $\mu_{l0}$  and  $\mu_{v0}$  are the equilibrium chemical potentials of liquid and vapor,

The appropriate form of the Euler equation says:

$$I - \left( \frac{d\rho}{dx} \right) \left[ \frac{\partial I}{\partial (d\rho/dx)} \right] = 0 \quad (5)$$

where  $I$  represents the integrand of Cahn-Hilliard equation . If we apply the integrand of Eq. (5) in Eq. (4) [12], we obtain a differential equation whose solution is the composition profile corresponding to invariance value (maximum, minimum or saddle points) of the integral. The condition for invariance value is

$$\Delta\alpha(\rho) - \kappa \left( \frac{d\rho}{dx} \right)^2 = \text{const} \quad (6)$$

In this equation the constant value must be zero, and also both  $\Delta\alpha(\rho)$  and  $\frac{d\rho}{dx}$  tend to zero when  $x \rightarrow \pm\infty$ . Hence a minimum value of the surface tension can be expressed as:

$$\sigma = 2 \int_{\rho_v}^{\rho_l} [\kappa \Delta\alpha(\rho)]^{\frac{1}{2}} d\rho. \quad (7)$$

## 2.2 The Simha-Somcynsky (SS)-Eos Theory

Simha-Somcynsky (SS) developed an equation of state (EOS) based on the lattice-hole model[13] introducing the temperature and volume dependent occupied site fraction,  $y(V, T)$ . The occupied site fraction,  $y(V, T)$ , and the complementary hole fraction,  $h(V, T)$ , are given by the following equation:

$$y = 1 - h = \frac{sN}{sN + N_h} \quad (8)$$

where  $s$  is the number of segments in a molecule, and  $N$  and  $N_h$  are the number of molecules and holes respectively. The SS theory is formulated in terms of the



reduced volume, temperature and pressure, viz.:

$$\tilde{V} = V/V^*; \quad \tilde{T} = T/T^*; \quad \tilde{P} = P/P^* \quad (9)$$

where the scaling parameters are as follows:  $V^*$  is defined by molar volume  $sv^*$  of the molecule,  $T^*$  by  $q_z \varepsilon^* / ck$  as a balance between attraction and thermal energy contributed by the external degrees of freedom (where  $k$  is the Boltzmann's constant), and  $P^*$  is then assigned by the ratio between chain attraction energy  $q_z \varepsilon^*$  and volume  $sv^*$ . Here  $3c$  that appears explicitly in the equilibrium condition is the total degrees of freedom of molecule. In this article, we have considered the ideal chain flexibility employing  $3c = s + 3$ .

The configurational partition function for the ensemble can be written as

$$Z_{conf} = g(N, y) [\nu_f(y, V)]^{3c} \exp(-E_0(y, V) / kT) \quad (10)$$

where  $E_0$  is the total lattice energy of the system employed Lennard-Johns potential energy,  $\nu_f$  is the free volume, and  $g(N, y)$  is the combinatorial factor that is the total number of distinguishable degenerate arrangements of the holes and molecules by Boltzmann's equation. It can be calculated from the mixing entropy of an assembly of molecules and holes as

$$\Delta S_m = k \ln g(N, y) \quad (11)$$

Hence the combinatorial factor is expressed as

$$g(N, y) \propto y^{-N} (1-y)^{-sN(\frac{1-y}{y})}. \quad (12)$$

The SS-EOS equation, derived from the configurational Helmholtz energy, is

$$\frac{\tilde{P}\tilde{V}}{\tilde{T}} = \frac{1}{1-\zeta} + \frac{2y}{\tilde{T}} Q(1.011Q - 1.2045) \quad (13)$$

where  $Q = (y\tilde{V})^{-2}$  and  $\zeta = 2^{-1/6} y (y\tilde{V})^{-1/3}$ . The occupied site fraction can be obtained

from the minimization of the Helmholtz energy of an ensemble,  $\partial F / \partial y|_{\tilde{V}, \tilde{T}, c/s} = 0$

$$\frac{s}{3c} \left( \frac{s-1}{s} + \frac{\ln(1-y)}{y} \right) = \frac{\zeta - \frac{1}{3}}{1-\zeta} + \frac{y}{6T} Q(2.409 - 3.303Q). \quad (14)$$



Using the coupled Eqs. (13)-(14), we can determine the scaling parameters,  $P^*, V^*, T^*$ , and the structural parameter  $3c/s$ , which can be obtained by superimposing experimental  $P$ - $V$ - $T$  data on the theoretical  $\tilde{P}, \tilde{V}, \tilde{T}$  surface. Having these parameters at hand, we can compute the hole fraction,  $h(V, T) = 1 - y$ , of the lattice model (as a measure of the free volume [14]).

For a binary system (occupied and unoccupied), Gibbs free energy of mixing  $\Delta G_m$  for the a thermal condition (leading to enthalpy of mixing  $\Delta H_m = 0$ ) is defined as

$$\Delta G_m = -T\Delta S_m = kTN \left[ \ln y + \frac{s(1-y)}{y} \ln(1-y) \right] \quad (15)$$

where the right hand side is obtained by substituting Eq(11) with Eq(12). The chemical potential of the system is given by

$$\mu = \frac{\partial \Delta G_m}{\partial N} = \frac{\partial \Delta G_m}{\partial y} \bigg|_N \frac{\partial y}{\partial N} + \frac{\partial \Delta G_m}{\partial N} \bigg|_y = kT \left( -(1-y)(s-1) + \ln y \right). \quad (16)$$

We can then write the chemical potential difference between the surfaces:

$$\Delta \mu = \mu_b - \mu_s = kT \left[ (y_b - y_s)(s-1) + \ln \left( \frac{y_b}{y_s} \right) \right] \quad (17)$$

where the indices  $b$  and  $s$  refer to bulk and surface. On the other hand the scaled  $\Delta \tilde{\alpha}$  is expressed in terms of chemical potential difference as

$$\Delta \tilde{\alpha} = \tilde{\rho} \Delta \tilde{\mu} = C^{-1} y \Delta \tilde{\mu} \quad (18)$$

where the right hand side of Eq(18).is obtained by substituting Eq(16). Substituting Eq. (18) into Eq. (7)., the scaled surface tension can be written as

$$\tilde{\sigma} = \frac{2}{\sqrt{C}} \int_{1-y}^y \left( \tilde{\kappa} \Delta \tilde{\mu} \right)^{\frac{1}{2}} dy \quad (19)$$

where the reduced variables are

$$\Delta \tilde{\alpha} = \Delta \alpha / P^*, \quad \tilde{\sigma} = \sigma / \sigma^*, \quad \tilde{\kappa} = \kappa / \kappa^* \quad (20)$$

and the scaling parameters are

$$\sigma^* = q_z \varepsilon^* v^{*-2/3}, \quad \kappa^* = \frac{q_z}{m_0^2} v^{*5/3} \varepsilon^* \quad \text{and} \quad x^* = \sqrt{\frac{\kappa^*}{c_{yV}^* \mu^*}}. \quad (21)$$





where  $\tilde{x}_0$  and  $\rho_v$  represent an arbitrarily chosen origin and vapor density. The  $x$  origin is arbitrarily located at a density of  $(\tilde{\rho}_l + \tilde{\rho}_v)/2$ . A distance  $\tilde{x}$  may be determine for any  $\rho$  lying between the bulk densities by evaluating the integral in Eq. (22) numerically[14].

Now we can write the density depth profile in terms of the occupied site fraction,  $y$ , by means of Eq.(17) we get :

$$\tilde{x} = \tilde{x}_0 + \frac{1}{\sqrt{C}} \int_{1-y}^y \left( \frac{kT}{\tilde{\kappa}} \left( (y_b - y_s)(s-1) + \ln \left( \frac{y_b}{y_s} \right) \right) \right)^{-1/2} dy \quad (22)$$

polyethylglycol (PEG302,PEG692 and PEG18500) which was fitted for temperature range of (313-473) K and pressure range of 0.1-150MPa for polyethylene lglycol as written above. The SS theory employs these calculated specific density data to obtain the characteristic parameters viz. the scaling pressure, scaling temperature and scaling volume. These parameters are simultaneity fitting of the density data with the theory using the coupled Eqs. (13)-(14). Table1 shows these computed parameters with the average and maximum relative percentage error in volume given by

$$\% \Delta V = \frac{100}{N} \sum \frac{V_{theory} - V_{exp}}{V_{exp}} \quad (23)$$

Where  $V_{theory}$  is the specific density calculated from the SS theory and  $V_{exp}$  is the one calculated from the Tait equation, and  $N$  is the number of data. The theory with these parameters given in Table 1 is well described with the average percentage error in volume( $\Delta V$ ) 0.03%, and maximum percentage error in volume( $\Delta V_{max}$ ) 0.28%.



### 3. Results And Discussion

PARAMETERS	PEG302	PEG692	PEG18500	REF NO.

Some important thermodynamics parameters of polyethylene glycol that has used in this work as in table 1 employed to extract the list of data has been used to draw the density profile.

**Table1: The Scaling Parameters that obtained as a result of the SS and CH Theories**



$T_c(K)$	864.85	868.40	962.58	[7]
$\sigma_o(mN / m)$	75.08	74.93	69.01	[7]
$P^*(Mpa)$	1080	1038	1035	[7]
$V^*(cm^3/gr)10^{-3}$	0.8507	0.8668	0.8688	[7]
$T^*(K)$	9274	9138	9268	[7]
$\varepsilon^*(K)$	389	386	390	our study
$\sigma^*(erg / cm^2)10^{-2}$	9.70	5.40	0.60	our study
$K^*(erg.cm^5/gr^2)10^{-4}$	0.44	1.79	431	our study
$C$ (External Freedom Degree)	3.6	8.2	216	our study
$m_o(g)$	36.06	36.04	36.05	our study
$s$ (Number of segment)	8	19	513	our study
$\% \Delta V$	0.03	0.03	0.04	our study
$\% \Delta V_{max}$	0.28	0.16	0.12	our study

We noted  $T^*$  increase when increased chain length. The characteristic parameters  $V^*$  relatively fluctuations at nearest points and  $p^*$  decrease when chain length increasing. The reduced surface tension  $\tilde{\sigma}$  is increase while increasing molecular weight of polyethylene glycol. Finally the parameter gradient energy coefficient  $\tilde{\kappa}$  is increase in linearity with increasing molecular weight of polyethylene glycol

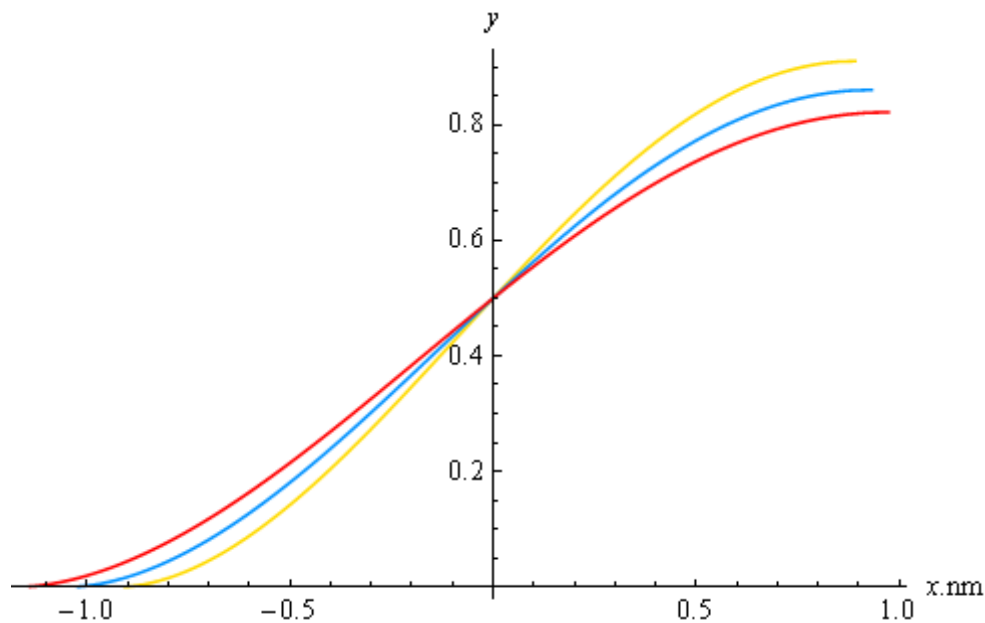
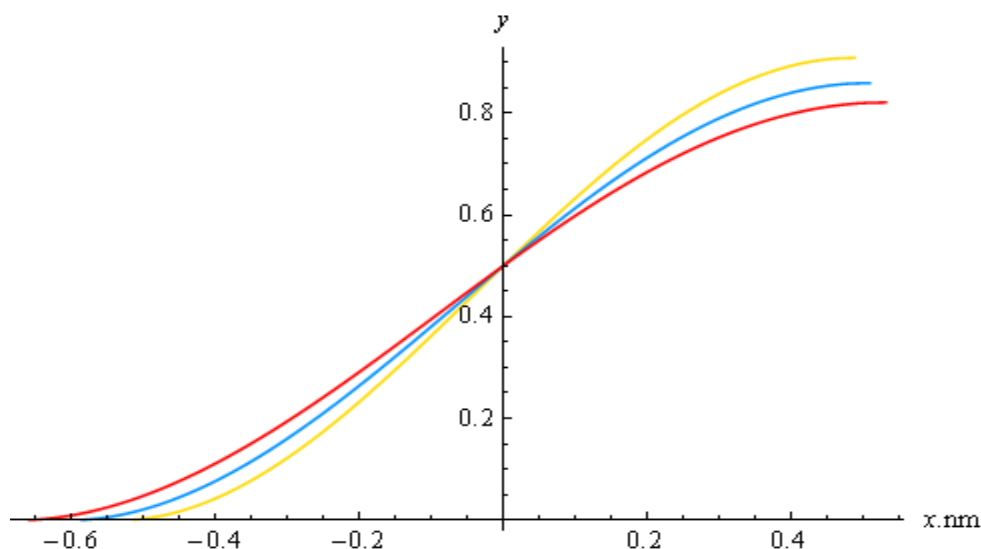
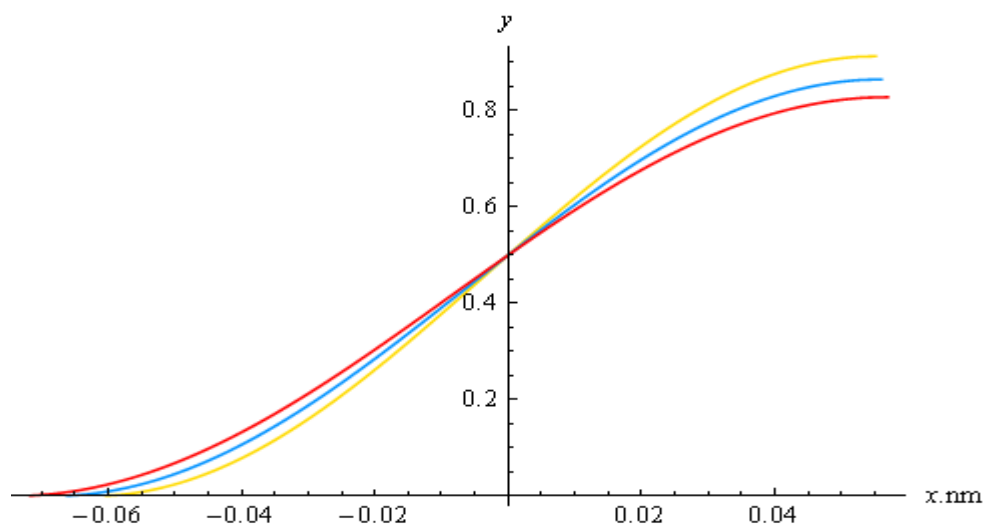


Figure1 ( yellow line 333K, blue line 413 K, red line 473 K ) The density profile of polyethylene glycol and interface thickness of PEG302 is 2nm approximately



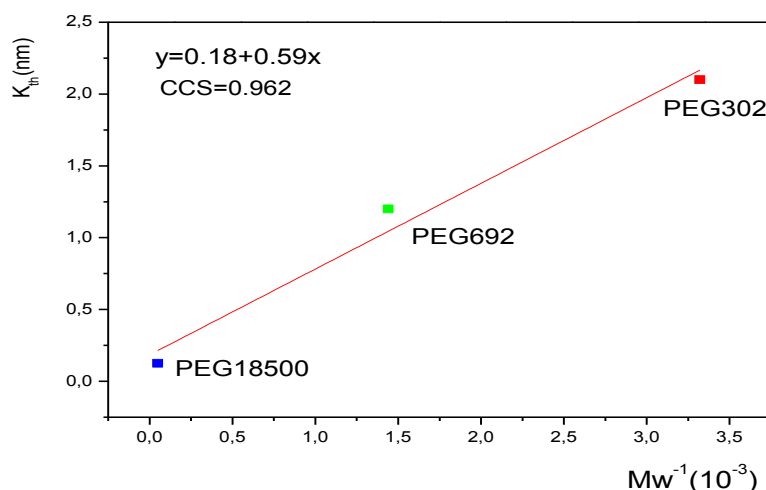
**Figure1**

( yellow line 333K, blue line 413 K, red line 473 K ) The density profile of a polyethylene glycol and interface thickness of PEG692 is 1.2nm approximately



**Figure3:(** yellow line 333K, blue line 413 K, red line 473 K ) The density profile of a polyethylene glycol and interface thickness of PEG18500 is 0.12nm approximately

From the figures 1, 2 and 3 we have get the data information of interface thickness of polyethylene glycol according with its molecular weight as 2nm '1,2nm and 0.12 nm



**Figure4: Showing the relation of inverse molecular weight with interface thickness of polyethylene glycol at different molecular weight.**

The data of the figure4 that we have get it from the density profiles in figures (1,2 and 3),the x-axes from the mentioned figures that represented the interface thickness as a function of molecular weight for polyethylene glycol, we see the increasing in molecular weight leads to decreasing in interface thickness of polyethyleneglycol.

### **Discussion:**

The polymer materials studied in this article are polyethylene glycol (PEG302, PEG692, and PEG18500). Figure( 1) shows the red line at temperature 473 K which starts more deeper inside from the bulk as a result of expansion that happened in surface layer, then the blue line starfs because the temperature of the blue line is less than that of the red line which is 413 K. Finally the yellow line starts at temperature 333 K. This event is seen at different molecular weight in polyethylene glycol which is mean that the temperatures mentioned above is above the glass transition temperature ( $T_g$ ). Another remarkable observation in the figures (1, 2 and 3) the interface thickness as a function of molecular weight . The surface or interface thicknesses were found for PEG302 to be 2.1 nm , for PEG692 is 1.2 nm and for PEG18500 to be 0.12 nm approximately. When the molecular weight increase the surface or interface thickness decreases . From the figures (1, 2 and3) we



observe that when approaching the surface region of a polymer the hole fraction to increase. This idea is certified by Simha-Somcynsky (SS) and Cahn-Hilliard (CH). In the bulk material the mobility of the polymer chains can be interpreted by of free volume or occupied site fraction,  $y(V, T)$ . Remembering that the important correlation between surface tension and molecular weight of polymers is  $\sigma(M_n) = \sigma_\infty - R/M_n$  where  $\sigma_\infty$  represents the value of  $\sigma(M_n)$  at infinite molecular weight, and  $R$  is a constant. Some low molecular weight polymers correlate well when  $M_n^{-2/3}$ . It is clearly from surface tension formula that increasing molecular weight leads to increase in surface tension. The molecular weight mentioned above also important to constitute the range of thickness of interfaces. So we see different interface range or thickness for different polyethylglycol (PEG302, PEG692, PEG18500). From the depth density profile we could to certificate the reverse correlation between interface thickness and molecular weight of polymer (polyethylglycol). When increasing the surface thicknesses decreasing for values are (PEG302  $\approx$  2nm, PEG692=1.2nm, PEG1800=0.12nm approximately). We obtain interface thickness ( $Int_{th}$ ) [15] which is given in form  $Int_{th} = 2a / (6\chi)^{1/2}$ . Where  $Int_{th}$  represent interface thickness,  $a$  is the statistical segment length and  $\chi$  represent the Flory-Huggins interaction parameter. Another spectacular phenomena in the density profile of polyethylene glycol (PEG302, PEG392 and PEG18500) is that when increasing the temperature the slipping at surface is observed which leads to extension in surface thickness of the polyethylene glycol. Finally the Simha-Somcynsky that is used for the first time in conjunction with Cahn-Hililard theory to extractd the density profile of polyethylene glycol.

#### 4.CONCLUSION

- 1- Has been certified the hole fraction increase from bulk to surface or interface .
- 2-Only a very small fraction of the polyethylene glycol chains are close enough to a surface in order for their physical state and behavior are different.

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[kirkukjournsci@gmail.com](mailto:kirkukjournsci@gmail.com)



- 3- By increasing the temperature the surface layer stretched (extended) then the density profile starting from depth as in a red line (473K).
- 4 When increasing the molecular weight leads to decreasing the interface thickness which is the polyethylene glycol polymer is quite homogenous.
- 5- The most of the polymers component is immiscible to blending, So main reason belong to multiphase, our the best conclusion from this study the high degree of polymerization, It will help us to innovation the new polymers.. Because the high degree of polymerization reducing ( eliminating) the different phases..

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