

STUDYING THE GRADIENT ENERGY COEFFICIENT S AS FUNCTION OF MOLECULAR WEIGHTS

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Abstract: In this research, polyethylene of different molecular weights (PE198, PE507, PE619, PE110) were studied using the Simha-Somcynsky (SS) theory with the Cahn-Hilliard (CH) theory together extracting the physical properties of these polymers as the energy gradient in detecting and innovation new polymers in these polymeric materials play an important role in detecting new polymers and the surface tensile of the polymer is closely eliminate is related with the gradient energy coefficient with as a function molecular weights and temperatures. We have been extracted the state equation for the polymers material system and they had been obtained the minimum and maximum error in volume by using the Newton Raphson method to obtain the volume of external freedom under pressure (1-150) MPa and up to 513K to temperature the minimum and maximum error in volume ratio for PE1100 was (0.014518) and (1.4148) for PE198 respectively

THEORIES

Cahn-Hilliard Theory

The Cahn-Hilliard equation holds significant importance in the field of materials science. It is a conservation law where the average parameter, corresponding to atomic density, is maintained. Numerous articles have been dedicated to the mathematical and numerical studies of this equation. The Cahn-Hilliard theory describes the free energy profile of polymer surfaces or interfaces as a heterogeneous mixture with several phases. The total free energy of the liquid polymer system consists of contributions from two types: one from the homogeneous region and the other from the heterogeneous region. The composition gradient's contribution to the free energy is indicated by the gradient energy coefficient, denoted by κ .

The interface between two non-condensed phases and the system's thermodynamic properties are related, according to the Cahn-Hilliard theory. When considering a binary alloy in a two-phase equilibrium, the density gradients of the heterogeneous system continuously vary from the bulk density or liquid density to the surface or vapor density. This means the Helmholtz free energy density, α , of a system with an interface can be obtained by expanding the Helmholtz free energy in a Taylor series around the equilibrium state.

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$$\alpha(\rho, \nabla\rho, \nabla^2\rho \dots) = \alpha_0(\rho) + k_1 \nabla^2\rho + k_2 (\nabla\rho)^2 \quad (1)$$

$\alpha_0(\rho)$ represents the local free energy density for the parameter of the homogeneous Laplacian polymer system and the heterogeneous region of the system, respectively, in terms of gradient density as follows [7].

$$k_1 = \left(\frac{\partial \alpha}{\partial \nabla^2 \rho} \right)_0 \quad (2)$$

$$k_2 = \frac{1}{2} \left(\frac{\partial^2 \alpha}{\partial (\nabla \rho)^2} \right)_0 \quad (3)$$

In equations (3, 2), the subscript (o) indicates derivatives limited to the magnitudes $(\nabla\rho)$ and $(\nabla^2\rho)$ heading towards zero. Where the free Helmholtz energy, starting with A, making it of total volume V, is determined by:

$$A = \int [\alpha_0(\rho) + k (\nabla\rho)^2] dV \quad (4)$$

The potential difference in the interaction between the surface and the bulk is represented by (K), which determines the gradient energy coefficient of the system in the previous equation. The local free energy of a homogeneous system is the first term in equation (No. 4), and the composition gradient contribution is the second term. in free energy [2, 10].

Now, we divide the last equation by the area to obtain the following expression for surface tension, which is the Helmholtz free energy equation in terms of surface tension (4) for a unit cross-sectional area of the interface, where x is the depth perpendicular to the interface.

$$\gamma = \int_{-\infty}^{\infty} [\Delta \alpha + k (\nabla\rho)^2] dx \quad (5)$$

$(\Delta \alpha)$ represents the difference between two-phase equilibrium mixtures with liquid and gaseous states and the Helmholtz free energy density of a homogeneous liquid with density (ρ) [11].

The deep point of the mass is represented as follows using Euler's equation:

$$I - \left(\frac{d\rho}{dx} \right) \left[\frac{\partial I}{\partial (d\rho/dx)} \right] = 0 \quad (6)$$

Therefore, equation (6) can be used and replaced in equation (5) [16], to gain a differential equation.

Cahn-Hilliard integral is determined by parameter (I)

$$I = \Delta\alpha + k(\nabla\rho)^2 \quad (7)$$

Equation (7) can be written in one dimension:

$$I = \Delta\alpha + k \left(\frac{\partial \rho}{\partial x} \right)^2 \quad (8)$$

Then equation (8) is applied in the Euler equation to get the following equation:

$$\Delta\alpha + k \left(\frac{d\rho}{dx} \right)^2 - \frac{d\rho}{dx} \left[2k \left(\frac{d\rho}{dx} \right) \right] = 0 \quad (9)$$

For the second and third terms of the equation, we use (k) as a common factor (9)

$$\Delta\alpha - k \left(\frac{d\rho}{dx} \right)^2 = 0 \quad (10)$$

It would be easy to write equation (10) as:

$$\Delta\alpha = k \left(\frac{d\rho}{dx} \right)^2 \quad (11)$$

The (dx) is extracted from equation (11) and written as follows:

$$dx = \left(\frac{\Delta\alpha_{(\rho)}}{k} \right)^{-1/2} d\rho \quad (12)$$

$\Delta\alpha_{(\rho)}$ Helmholtz's free energy as a function of density is referred to.

$$dx = k^{-1/2} \Delta\alpha_{(\rho)}^{-1/2} d\rho \quad (13)$$

Equation (13) becomes the following form:

$$\gamma = \int_{-\infty}^{\infty} [2 \Delta\alpha_{(\rho)}] dx \quad (14)$$

By substituting equations (13) into (14) we calculate the profile of surface density and surface tension according to which the given equation is represented:

$$\gamma = 2 \int_{-\infty}^{\infty} [k \Delta\alpha_{(\rho)}]^{1/2} dx \quad (15)$$

Model Equations for Cahn-Hilliard's Theorem

Let (Ω) be the domain of calculation by which the solution to the Cahn–Hilliard equation is determined. Suppose Ω is bounded by $\partial\Omega$. In this topic, first, the binary case is dealt with. Next, the multicomponent model is introduced, and we end with a stress-enhanced diffusion model.

Binary Case

We will treat the Cahn–Hilliard equation in more detail as a model of a diffuse interface. We assume that (c) is the mass fraction of a species in a binary system (that is, a system consisting of only two types), and then the total free energy of Ginzburg-Landau is given to the system [5, 8, 17].

$$F(c) = \int_{\Omega} \left\{ f(c) + \frac{\kappa}{2} |\nabla c|^2 \right\} dV \quad (16)$$

The Simha-Somcynsky (SS) Theory

In polymer molecules, monomers are the smallest units. These small units of the polymer molecules are collected in order to create a part of the polymer. In the network structure, the polymers are placed one after the other in order to create the statistics of the polymer [3, 9]. In the network structure there are filled and unfilled cells [12]. There are Slices of empty and completely filled cells in the same grid SS theory was applied to the structures of long and short polymers [6, 13, 15]. Specific

volume results [4] for filled and unfilled cells were obtained as below:

$$y = \frac{N_s}{N_h + N_s} = 1 - h \quad (17)$$

The location of the occupied part [4] represents its evaluation function [14] filled and unfilled cells

$$Z_{conf} = g(N, y) [v_f(V^{\sim}, y)]^{cN} \exp \left[\frac{E_0(V^{\sim}, T^{\sim}, y)}{kT} \right] \quad (18)$$

$$g(N, y) = y^{-N} (1 - y)^{-sN \left(\frac{1-y}{y} \right)} \quad (19)$$

The total power of the polymer lattice is E_0

$$E_0 = \frac{1}{2} y N q_z \varepsilon^* \left[A \left(\frac{v^*}{\omega} \right)^4 - 2B \left(\frac{v^*}{\omega} \right)^2 \right] \quad (20)$$

Here $\omega = yV/sN$ represents the value of the location of the occupied and non-occupied part or the value of the gap part [1],

$$v_f = v^* \left\{ y \left[(yV^{\sim})^{1/3} - 2^{-1/6} \right] + (1 + y)(yV^{\sim})^{1/3} \right\}^3 \quad (21)$$

The occupied cell's void is represented by the first part of the free volume in this instance, while the vacant cells in the lattice are represented by the second part. From the polymer lattice structure, the Helmholtz free energy [18] was obtained.

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

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

$$= -3kTcN \left\{ \ln \left[(yV^{\sim})^{1/3} - 2^{-1/6} \right] + \frac{1}{3} \ln(v^*) \right\} + \frac{1}{2} y N q_z v^* (yV^{\sim})^{-2} + \frac{1}{2} y N q_z v^* (yV^{\sim})^{-2} [1.011(yV^{\sim})^{-2} - 2.049] \quad (22)$$

Only at an equilibrium state, where the free energy derivative for y equals zero, does the occupancy rate of the system remain constant.

$$\left(\frac{\partial F}{\partial y} \right)_{V, T^{\sim}, \frac{c}{s}} = \frac{s}{3c} \left[\frac{s-1}{s} + \frac{\ln(1-y)}{y} \right] - \frac{\eta - \frac{1}{3}}{1-\eta} - \frac{y}{6T^{\sim}} (yV^{\sim})^{-2} [2.409 - 3.033 (yV^{\sim})^{-2}] = 0 \quad (23)$$

Here $\eta = 2^{-1/6} y(yV^{\sim})^{-1/3}$, We derive from the energy of Helmholtz for V the following equation is obtained [18].

$$P = \left(\frac{\partial F}{\partial y} \right)_T = P[V^{\sim}, T^{\sim}] = P[V^{\sim}, T^{\sim}; y(V^{\sim}, V^{\sim})] \quad (24)$$

$$\frac{P^{\sim} V^{\sim}}{T^{\sim}} = \frac{1}{1-\eta} + \frac{2y}{T^{\sim}} (yV^{\sim})^{-2} [1.011 (yV^{\sim})^{-2} - 1.2045] \quad (25)$$

The relationship between the theoretical and experimental PVT values and the

explicit expression of the reduced parameters [7] are given below.

$$P^{\sim} = \frac{P}{P^*}, V^{\sim} = \frac{V}{V^*}, T^{\sim} = \frac{T}{T^*} \quad (26)$$

Where,

$$P^* = \frac{cT^* R^*}{mV}, V^* = \frac{v^* S}{m}, T^* = \frac{q_Z \varepsilon^*}{c} \quad (27)$$

$$\left(\frac{P^* V^*}{T^*}\right) M_0 = \left(\frac{C}{S}\right) R \quad (28)$$

CONCLUSIONS AND DISCUSSIONS

Table 1: Shows the Unique Characteristics of Polyethylene at Various Molecular Weights.

maxErr	MinErr	T*(k)	V*(cc/gm)	P*(Mpa)	ε^* (k.K)	K* (erg.cm/ gr ²)	*V10 ⁶	C	S	Polymers
1.4148	0.01417	11490.5	0.00124531	715.396	149.7	0.000103166	17.646	1.85	14	PE198
0.397534	0.014082	18274.6	0.00123478	691.749	143.875	0.00046873	17.388	12.85	36	PE507
0.316869	0.0140718	18485.5	0.00122014	707.963	145.542	0.000648952	17.695	3.48	44	PE619
0.224046	0.0140518	2343.1	0.001231	678.688	140.845	0.00615247	17.2979	4.7	78	PE1100

Table 2: Represents the Measurement Coefficients of Polymer Density Low Surface Tensile and Low Gradient Energy Coefficient Under Temperatures Starting From 313 K And 473 K Obtained from Cahn-Hilliard Theory (CH) With FC Contribution at Different Molecular Weights.

κ/κ^*	γ'/γ	P(kg/m ³)	T(k)	Polymers
0.128131	0.601729	748.487	313	PE 198
0.0467996	0.259593	626.893	473	
0.34972	1.55997	798.289	313	PE 507
0.1644	1.0443	704.735	473	
0.39407	1.81568	809.923	313	PE 619
0.19144	1.22628	717.272	473	
0.49613	2.82823	816.205	313	PE 1100
0.22367	1.88607	732.535	473	

Table 3: shows the values of the hole part (gap) (h=1-y) for different molecular weights at temperatures from K313 K to 413 K.

PE 1100	PE 619	PE 507	PE 198	T(k)
0.06277	0.7488	0.07722	0.120694	313
0.08459	0.08683	0.08943	0.136927	333
0.09606	0.09916	0.10203	0.153554	353
0.10788	0.12284	0.11497	0.170561	373
0.11997	0.12482	0.12825	0.187941	393
0.11997	0.13811	0.14182	0.205694	413

Table 4: shows the values of the location of the occupied part of different molecular weights at temperatures from 313K to 513K.

PE 1100	PE 619	PE 507	PE 198	T(k)
0.932802	0.9361152	0.936163	0.943363	313
0.933071	0.93632	0.936327	0.94365	333
0.933182	0.936474	0.936479	0.943952	353
0.933286	0.936623	0.936626	0.944274	373
0.933389	0.936772	0.936775	0.944622	393
0.933494	0.936926	0.936929	0.944999	413
0.93372	0.937087	0.937092	0.94541	433
0.933318	0.937258	0.937266	0.945859	453
0.933351	0.937442	0.937454	0.94635	473
0.933373	0.937641	0.937657	0.946889	493
0.933361	0.937856	0.936968	0.947481	513

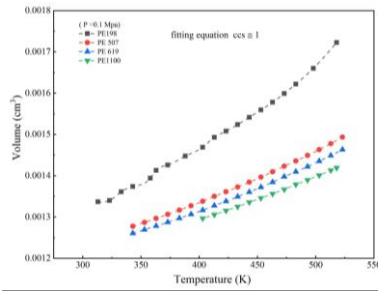


Figure 1: Shows the Values of (T) For Different Molecular Weights of Polyethylene as A Function of the Specific Volume at A Pressure of 0.1Mpa.

Figure 1 shows that temperatures increase with increasing volume with constant pressure, as it affects the movement of polymer molecules and causes particle divergence, and this is one of the reasons for structural imbalance and increasing the gap part.

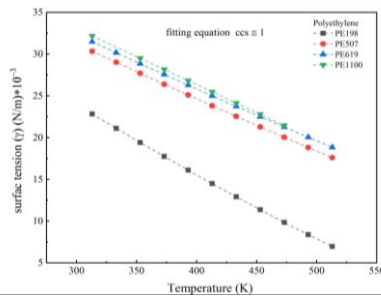


Figure 2: Shows the Relationship Between Temperature and Surface Tension Coefficient for Polymers with Different Molecular Weights (PE198, PE507, PE619, PE1100)

This data was extracted in the drawing using SS theory for dynamic properties, especially surface tension in the temperature ranges from 313 to 513. As the temperature increases, the average gap fraction rises, increasing the average gap fraction and, consequently, the surface tension, which is already softer. This is shown in Figure 2.

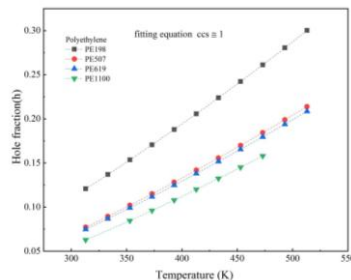


Figure 3: Values (T) for Different Molecular Weights of Polyethylene as A Function of the Gap Part.

The diagram in Figure 3 above shows small differences that occur at high pressure and

low temperatures, while at high temperatures and low pressure, the gap part is larger than in other areas. The gap part expands and increases at high temperatures.

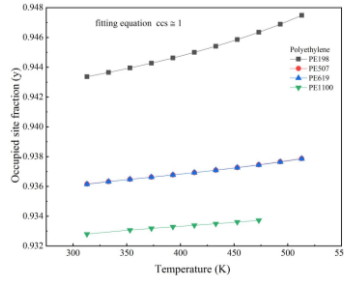


Figure 4: Relationship Between Temperature and Location of Occupied Part of Polymers of Different Molecular Weights (PE198, PE507, PE619, PE1100).

In the Figure 4, when the temperature increases, the gap part and the specific size increase, and the surface tensile coefficient decreases, the polymer becomes softer and the cell expands, and thus the occupier part decreases.

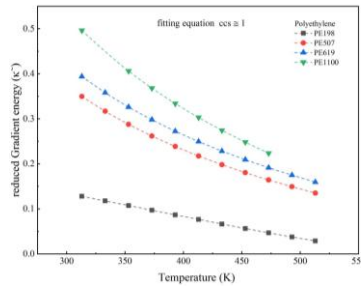


Figure 5: Shows the Values of Temperature and Low Gradient Energy Coefficient with Different Molecular Weights Polymers (PE198, PE507, PE619, PE1100).

Figure 5 shows the effect of temperature on the low gradient coefficient when the temperature decreases the specific volume and the unfilled part in the cell is caused by an increase in surface tension, which increases the low temperature coefficient.

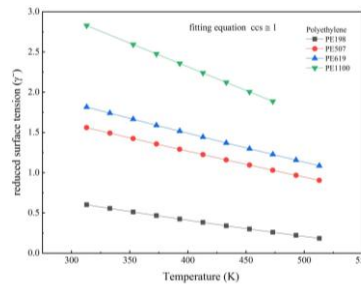


Figure 6: Shows the Relationship of Temperature and Coefficient of Surface Tensile Drop of Polymers (PE198, PE507, PE619, PE1100).

The value of the surface tensile drop coefficient is raised by reducing the temperatures which makes the polymer particles complex and become more rigid

and decrease in free volume and average gap part (see Figure 6).

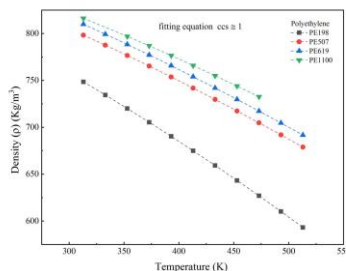


Figure 7: Shows the Relationship Between Temperature and Density of Polymers (PE198, PE607, PE619, PE1100).

Figure 7 shows the experimental data and the values calculated theoretically according to the theory of SS polymer density increases when the temperature decreases where the pressure increases and the free volume decreases and according to the theory of SS refers to the randomness in the distribution of particles in the lattice

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