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Theoretical Study of Polyethylene Crystallization Using Modified Weighted Density Approximation (MWDA)

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In this article, the crystallization of polyethylene is investigated by the modified weighted density approximation. Also, a direct correlation function of polyethylene based on the RISM theory is used. The free energy of a polyethylene is calculated using the density functional theory. The crystallization and also the solid and liquid densities of polyethylene are calculated and compared with the PRISM simulations and experimental results. It is shown that the results obtained by modified weighted density approximation (MWDA) are in a better agreement with the experimental results rather than the PRISM simulations.

INTRODUCTION

A polymer is a large molecule that is made by linking the repeating units. The crystallization ability of polymers has a very important industrial application [1]. Most of the factors affecting the crystallization rate of polymers are polymer chain structure, molecular weight, the ability to form a secondary valence band and the thermal history of the polymer during construction. It is difficult to take into account all of the above factors in calculations and it will increase the number and variety of studying methods. Under certain conditions, most of the polymers will be crystallized into FCC lattice and acquire special properties. Many efforts have been taken to explain this phenomenon [2]. Structural properties and phase transition are the most important properties in the study of crystallization in polymers.

Many analytical methods have been developed to describe the structural properties and phase transition of many-body particle systems: Flory lattice [3-5], growth theories [6,7], Monte Carlo simulation [8-10], Landau-de Gennes theory [11] and density functional theory [12-16]. The density functional theory in the form of classical [12]

and quantum [13] is used to study different thermodynamic properties of simple liquid.

This theory is used to study homogeneous [14-16] and inhomogeneous systems such as limited liquid, liquid-solid interface [17,18], crystals [19-21], electron cloud distribution in atoms [22], phonon dispersions of cluster crystals [23], calculations of the electronic structure in atoms [24], the electronic structure of solids [25], and phase transition [26]. The basic assumption to study the phase transition in all of density functional theories is that the thermodynamic potential of a non-uniform system is approximated to its equivalent uniform system. The details of approximations used in relations distinguish each theory of the others. Therefore, different approaches have been used earlier. The approximations proposed by Rama Krishnan and Yussouff (RY) could be an example for these approximations [27].

This approximation is a suitable method to study freezing transition on simple and mixed liquid [28,29]. Another approximation in this field is a weighted density approximation (WDA) [30-34]. This approximation will lead to a better result compared to RY approximation [35-38]. Unfortunately, long and complicated calculations of this method made it very difficult. Therefore, we presented

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modified weighted density approximation (MWDA) [39,40] because this method will lead to better results and, since this method uses classical approximation, calculations in this method are more simple [41]. Some efforts were made in using density functional theory to explain polymers that a few of them can be mentioned.

Yethiraj and Woodward presented a density functional for polymer based on WDA theory [42]. A few years later, Yethiraj corrected his own theory by using complex weighted functional [43]. He studied two models in his article: A freely jointed hard chain model and a fused-sphere hard chain model. He used correlation function obtained from the polymer reference interaction site model (PRISM) and Ornstein-Zernike equations for polymer to start his calculation. Different studies have been conducted on polymers, especially polyethylene, with density functional method [44,45]. As an example, McCoy *et al.* studied polymer system by density functional [46]. One of the models of density functional theory is simple liquid model. This article indicates that simple liquid model can be used for polymers.

In this paper, at first, we calculate the correlation function of polyethylene (N = 6429) by curve fitting of experimental correlation function in [46]. Then, we calculate different parameters of polyethylene such as solid and liquid phase densities, Lindemann criterion, chemical potential, monomer diameter and isothermal compressibility of the liquid phase of polyethylene. After that, we compare our results with experimental ones and the results of different methods. Finally, we show that our results of MWDA method have a better agreement with experimental results in comparison with more complex methods such as Monte Carlo simulation or WDA, *etc*. Therefore, for the first time, we show that different parameters of polyethylene by MWDA method can simply calculated by using correlation function.

THEORETICAL FORMALISM

Weighted Density Functional Formalism

The basis of density functional theory is determining a grand free energy $\Omega[\rho]$ as an individual function of single-particle density $\rho(\vec{r})$. The goal of this part is to investigate thermodynamic properties of homogeneous systems.

At first, the grand free energy $\Omega[\rho]$ is obtained as [43]:

$$\Omega[\rho] = F[\rho(\vec{r})] + \int d\vec{r}\rho(\vec{r})[V_{ext}(\vec{r}) - \mu] \tag{1}$$

where μ is chemical potential, $V_{ext}(\vec{r})$ is the external potential and $F[\rho(\vec{r})]$ is single particle Helmholtz free energy functions of classical many-body system. The equilibrium density of the system is calculated by minimizing $\Omega[\rho]$ with respect to $\rho(\vec{r})$ in DFT method. The macroscopic properties of the system are calculated in an equilibrium state [43].

$$\frac{\delta\Omega[\rho]}{\delta\rho(\vec{r})} = 0 \tag{2}$$

The equilibrium Helmholtz free energy of the system can be calculated as [12]:

$$F[\rho_0] = F_{int}[\rho_0] + \int \rho_0(\vec{r})V_{ext}(\vec{r})d\vec{t} \tag{3}$$

where $F_{int}[\rho_0]$ is intrinsic Helmholtz free energy of the system. Therefore, from Eq. (2) we have [12]:

$$\mu = \mu_{int}[\rho_0,\vec{r}] + V_{ext} \tag{4}$$

Where μ_{int} is the intrinsic chemical potential and it is calculated as [12]:

$$\mu_{int} = \frac{\delta F[\rho]}{\delta(\rho)}\bigg|_{\rho=\rho_0}$$

Also the Helmholtz free energy of a classical many-body system is obtained as [43]

$$F[\rho(\vec{r})] = F_{id}[\rho(\vec{r})] + F_{ex}[\rho(\vec{r})] \tag{5}$$

where $F_{id}[\rho(\vec{r})]$ is the ideal part (It is the contribution of ideal gas) and $F_{ex}[\rho(\vec{r})]$ is the excess part (It is contribution of molecular interactions). It is a standard method to calculate Helmholtz free energy $F[\rho]$ that separates ideal part $F_{id}[\rho(\vec{r})]$ and makes some approximations for the excess part $F_{ex}[\rho(\vec{r})]$. The ideal part is calculated as [43]:

$$F_{id}[\rho(\vec{r})] = \beta^{-1} \int d\vec{r}\rho(\vec{r})[\ln\rho(\vec{r}) - 1] + \int d\vec{r}V_{int}(\vec{r})\rho(\vec{r}) \qquad (6)$$

with $V_{int}(\vec{r})$ being intramolecular interaction. The second term in Eq. (6) can be neglected because long-range effect is negligible in MWDA and WDA.

The excess Helmholtz free energy $F_{ex}[\rho]$ of a classical many-body system is a unique function of density and it is shown below [36]:

$$F_{ex}[\rho] = \int d\vec{r}\rho(\vec{r})\phi_{ex}(\vec{r};[\rho]) \qquad (7)$$

where $\phi_{ex}(\vec{r};[\rho])$ is the excess free energy per particle. In weighted density functional approximation, $F_{ex}[\rho]$ is obtained as [36]:

$$F_{ex}^{WDA}[\rho] = \int d\vec{r}\rho(\vec{r})\varphi_0\overline{\rho}(\vec{r}) \qquad (8)$$

Where φ_0 is the excess free energy per particle of homogeneous liquid, $\overline{\rho}(\vec{r})$ is the mean weighted density per particle $\rho(\vec{r})$ regarding weighted functional ω and it is calculated as follows [36]:

$$\overline{\rho}(\vec{r}) = \int d\vec{r}'\rho(\vec{r}')\omega[\vec{r}-\vec{r}';\overline{\rho}(\vec{r})] \qquad (9)$$

Weighted functional satisfies a normalization condition:

$$\int d\vec{r}'\omega[\vec{r}-\vec{r}';\overline{\rho}(\vec{r})] = 1 \qquad (10)$$

Also, the relationship between correlation functions of N particles and $F_{ex}[\rho]$ is defined as below [36,47]:

$$C^{(n)}(\vec{r}_1,...,\vec{r}_n;[\rho]) = -\frac{\delta^n\beta F_{ex}[\rho]}{\delta\rho(\vec{r}_1)...\delta\rho(\vec{r}_n)} \qquad (11)$$

Modified Weighted Density Approximation

In this article the modified weighted density functional approximation is used because it is simple and is in a better agreement with simulations [47]. The weighted density approximation method is approximated for $\phi_{ex}(\vec{r};[\rho])$. This method makes it possible to calculate the localized excess free energy per particle. Also, the formulation focuses on excess free energy per particle $\beta F_{ex}/N$; in modified weighted

density approximation method, which N is the number of particles of the system. Since $F_{ex}[\rho]/N$ does not depend on the position of the particle compared with $\phi_{ex}(\vec{r};[\rho])$, we show the weighted density by $\hat{\rho}$ that the difference between it and $\overline{\rho}(\vec{r})$ is its independence position.

The approximation used in the calculation of $F_{ex}[\rho]/N$ can be written as [36]:

$$F_{ex}^{MWDA}[\rho]/N = \varphi_{ex}(\hat{\rho}) \qquad (12)$$

where:

$$\hat{\rho} \equiv \frac{1}{N}\int d\vec{r}\rho(\vec{r})\int d\vec{r}'\rho(\vec{r}')\tilde{\omega}(\vec{r}-\vec{r}';\hat{\rho}) \qquad (13)$$

The weight density functional satisfies the normalization condition in Fourier space [48]:

$$\tilde{\omega}(k;\rho_0) = \frac{-1}{2\varphi'(\rho_0)}[\beta^{-1}C^{(2)}(k;\rho_0) + \delta_{k,0}\rho_0\varphi_0''(\rho_0)] \qquad (14)$$

The weighted density $\hat{\rho}$ must be calculated for the study of the Helmholtz free energy. This calculation is simple in Fourier space, because in Eq. (13) the volume integrals are converted to summation in inverse lattice vectors [48]:

$$\hat{\rho} = \frac{1}{N}\int d\vec{r}\rho(\vec{r})\int d\vec{r}'\rho(\vec{r})\,\omega(\vec{r}-\vec{r}';\hat{\rho}) = \rho_s + \frac{1}{\rho_s}\sum_{G\neq 0}\rho_G^2\,\omega_G(\hat{\rho}) \qquad (15)$$

where ρ_s is mean solid density, ρ_G and $\tilde{\omega}_G$ are a Fourier component of solid density and weighting function, respectively, at which Fourier component is related to mean solid density through $\rho_G = \rho_s e^{-G^2/4\alpha}$.

We can assume that $\rho_s(\vec{r})$ is focused as a summation of normalization of Gaussian on the $\vec{R}$ situation of lattice in FCC lattice. Therefore $\rho_s(\vec{r})$ can be written as [36]:

$$\rho_s(\vec{r}) = (\frac{\alpha}{\pi})^{3/2}\sum_R \exp[-\alpha(\vec{r}-\vec{R})^2] \qquad (16)$$

where α is localized parameter and is zero for homogeneous liquid limit and atoms are localized in liquid-to-solid phase

transition with the α increase. $\hat{\rho}$ can be written as the following replacing $\rho_G, \tilde{\omega}_G$ in Eq. (15) [48]:

$$\hat{\rho}(\rho_s, \alpha) = \rho_s [1 - \frac{1}{2\beta\varphi_0'(\rho)} \sum_{G \neq 0} \exp(\frac{-G^2}{2\alpha}) C^{(2)}(\vec{G}; \hat{\rho}) \tag{17}$$

The Helmholtz free energy per particle and direct correlation function is needed for calculation of $\hat{\rho}$. In this article we used a direct correlation function of polyethylene ($N = 6429$) [48,49]. φ_0 is defined *via* PY approximation as follows [48,49]:

$$\varphi_0(\eta) = (3/2)[(1/(1-\eta)^2) - 1] - \ln(1-\eta) \tag{18}$$

where $\eta = \pi\rho\sigma^3/6$

For calculation of ideal part, $F_{id}[\rho]/N$ can be written as [48]:

$$F_{id}[\rho_s] = \beta^{-1} \int d\vec{r}\rho_s(\vec{r})\{\ln[\rho_s(\vec{r})\lambda^3] - 1\} \tag{19}$$

For $\alpha > 50$, we can use the following equation [48]:

$$\frac{\beta F_{id}(\rho_s, \alpha)}{N} = \frac{3}{2}\ln\left(\frac{\alpha}{\pi}\right) + 3\ln(\lambda) - \frac{5}{2} \tag{20}$$

That $\lambda = 0.006/\rho_s$ is heat wavelength of the system. The Helmholtz free energy per particle of classical many-body system is calculated as below with the calculation of $F_{id}[\rho]/N$, $F_{ex}[\rho]/N$ [48,49]:

$$\frac{\beta F}{N} = \frac{\beta F_{id}}{N} + \frac{\beta F_{ex}}{N} \tag{21}$$

In the liquid phase, we used the Carnahan-Starling approximation for calculation, because it is exactly against PY approximation for the liquid phase, therefore we can write [50]:

$$\varphi_\circ^{cs}(\eta) = \frac{2}{(1-\eta)} + \frac{1}{(1-\eta)^2} - 3 \tag{22}$$

$\beta F_{ex}/N$ is calculated by Eq. (14), and Eq. (22) for liquid phase. F_{id} is calculated replacing solid density by liquid

density in (19) for liquid phase and is integrated, which results in [36]:

$$\frac{F_{id}[\rho_s]}{V} = \beta^{-1}\rho_s\{\ln[\rho_s] - 1\} \tag{23}$$

RESULTS AND DISCUSSION

Direct Correlation Function of Polyethylene

The direct correlation function must be replaced with the potential of the systems in the density function theory formalism. The direct correlation function for the hard spheres potential [30-36], Lennard-Jones potential [51] *etc.* has been calculated earlier. In this paper, the direct correlation function is calculated using Fig. 1 for polyethylene [46]. We calculated the direct correlation function $C(r)$ and Fourier transform it $C(k)$ using experimental Curve Fitting polyethylene $N = 6429$ [46].

Now, the direct correlation function as a polynomial of degree 3 is obtained by drawing the function, fitted with an error of less than 0.03, as shown in Fig. 1. First, we write the correlation function as a polynomial of degree 3:

$$C(r) = a + b(r/\sigma) + c(r/\sigma)^2 + d(r/\sigma)^3 \tag{24}$$

where a = -2.70000, b = 47.27416, c = -278.34645 and d = 484.09578, then using Fourier transformation and replacing ρ by η, correlation function is obtained Fourier transform as:

$$C(k) = 48[-b/k^4 + 12d/k^6]\eta \tag{25}$$

Figure 2 shows Fourier transforms of the correlation function.

Diameter of Monomers in Polyethylene

We studied a lot of $C(r)$, $C(k)$ and found that the best agreement of MWDA method for hard sphere diameter Is $\sigma_{CH2} = 3/7$ $A°$. According to the experimental results of σ_{CH2}, Chandler result [52] was $\sigma = 3/7$ $A°$, Slonimskii result [53] was $\sigma = 4/92$ $A°$, which as you can see, our results are in better agreement with experimental results. The exact amount of the monomer calculated by X-Ray and $\sigma = 3/90$ $A°$ that it has calculated with McCoy [46]. The results are
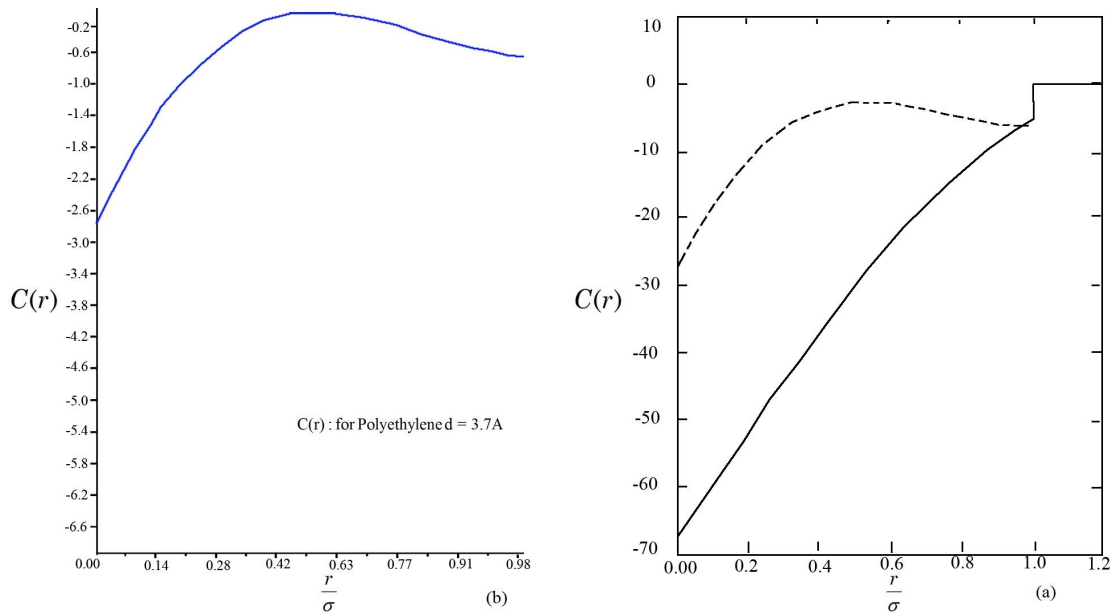
$C(r)$

$C(r)$

$C(r)$: for Polyethylene d = 3.7A

$\dfrac{r}{\sigma}$

(b)

$\dfrac{r}{\sigma}$

(a)

Fig. 1. (a) Direct correlation function for polyethylene (dashed line; polymer RISM theory; $T = 413 \,°K$ and hard spheres solid line; Percus-Yevick theory) at the phase transition [46]. (b) Fitness of Direct correlation function of polyethylene.
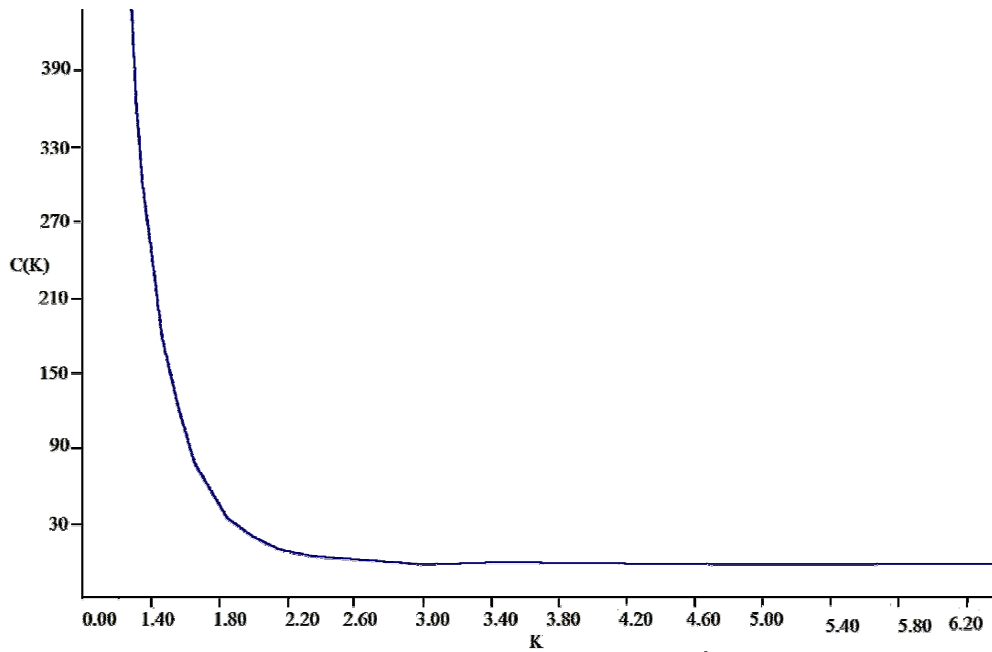

C(K)

K

Fig. 2. Plot $C(k)$ for crystallization of polyethylene ($N = 6429$, $\rho_s = 0.83$).

presented in Table 1 and in Fig. 1, at which we can compare own results whit McCoy result of the P-RISM method [46].

Liquid and Solid Phase Density of Polyethylene

At first, we selected $\rho_s = 0.9$ and changed it to 1.1 with 0.001 interval units. (Liquid freezing point ranges of hard sphere) [48,49]. After that we calculated lattice constant FCC $a = (4/\rho_s)^{1/3}$ as functions of ρ_s, and changed α from 1-250 with one interval units. Then, inverse lattice vector was calculated for 6200 consecutive shells using the calculated lattice constant in which the smallest vector $\vec{G}(1) = \frac{2\pi}{a}(1,1,1)$ is equal to $|\vec{G}(1)| = \frac{2\pi}{a}\sqrt{3}$. Then, initial $\hat{\rho}$ was selected and $\eta = \pi\hat{\rho}/6$ was calculated. After that, we calculated $C_\circ^{(2)}(\vec{G};\eta)$ for each $\vec{G}$ from 1-6200 [54,55].

$\varphi_\circ'(\hat{\rho})$ is obtained from differentiation of $\varphi_0(\eta)$ in Eq. (18) with respect to $\hat{\rho}$ and replacing η in that. Then, $\hat{\rho}(\rho_s,\alpha)$ is calculated with $\varphi_\circ'(\hat{\rho})$ in Eq. (17). Now, we calculate Eq. (17) as self constantly to give $\hat{\rho}$ with requested accuracy. Then, we obtain $F_{id}[\rho]/N$ by Eq. (20) and $F_{ex}[\rho]/N$ by Eq. (12). Finally, we calculated $\beta F/N$ by Eq. (21).

Figure 3 shows $\beta F/N$ as a function of α, which α is half the width of Gaussian. The minimum point in Fig. 3 shows equilibrium state of the system. Now, for liquid phase, we calculate $\beta F/N$ using φ_0 in Eq. (22) and we achieve $\beta F_{ex}/N$. Then, $\beta F_{id}/N$ is derived from Eq. (23). Finally, we calculate Helmholtz free energy per particle for the liquid phase of Eq. (21).

Figure 4 shows free energy of solid and liquid phases of polyethylene ($N = 6429$) at the point of transition. The calculation of solid and liquid phase densities is carried out with two methods. In the first method, we found the tangent of two curves. The contact points of this tangent and two curves could be considered as solid and liquid phases in freezing point, respectively.

In the second method, we used the polynomial of degree 2 for free energy of solid and liquid phase curves. Hence, using these relations' differentiations, we calculate the chemical potential and then thermodynamic potential, according to the following equations [48,49]:

Table 1. The Results of Monomer Diameter of Polyethylene in Different Methods

Method	σ
Chandler [52]	3.70A$^\circ$
Slonimskii [53]	4.92 A$^\circ$
X-Ray diffraction [46]	3.90 A$^\circ$
This work (MWDA)	3.70 A$^\circ$

$$\frac{\mu(P)}{V} = \frac{\partial}{\partial\rho}\left[\frac{F(P)}{V}\right] \qquad (26)$$

$$w(P) = \frac{F(P)}{V} - P\mu(P) \qquad (27)$$

Equating Eq. (27) with Eq. (28) in the coexistence condition leads to [36]:

$$\begin{aligned}\frac{\mu(P_s)}{V} &= \frac{\mu(P_l)}{V}\\ w(P_s) &= w(P_l)\end{aligned} \qquad (28)$$

at which ρ_s and ρ_l are obtained by Eq. (28)

Isothermal Compressibility Coefficient of Liquid Phase of Polyethylene

We calculated the isothermal compressibility coefficient of the liquid phase of polyethylene in coexisting condition with crystallization phase in putting related diameter of hard sphere and thermodynamic pressure in isothermal compressibility coefficient relation and differentiating respect to density as follows [59]:

$$\beta P / \rho = (1+\eta+\eta^2-\eta^3)/(1-\eta)^3 \qquad (29)$$

For calculation of compressibility factor of polyethylene we

$$1/K_T = \rho(\partial p/\partial\rho) \qquad (30)$$

Finally, we have: $\beta/K_T = 0.77$
Table 3 shows our result compared with McCoy result. As
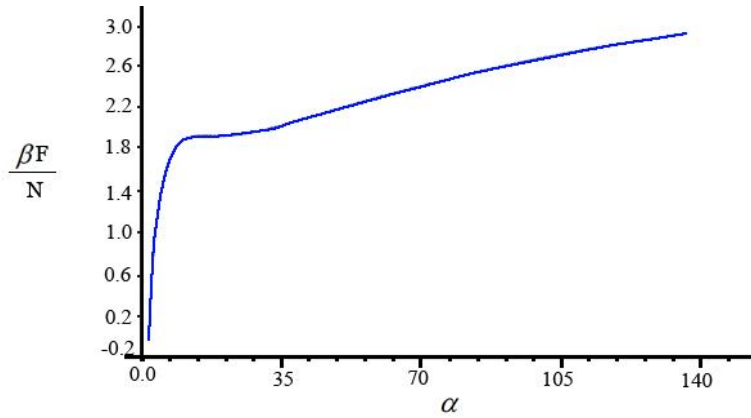
Fig. 3. The free energy of crystallization phase of polyethylene as a function of α ($\rho_s = 0.83$).
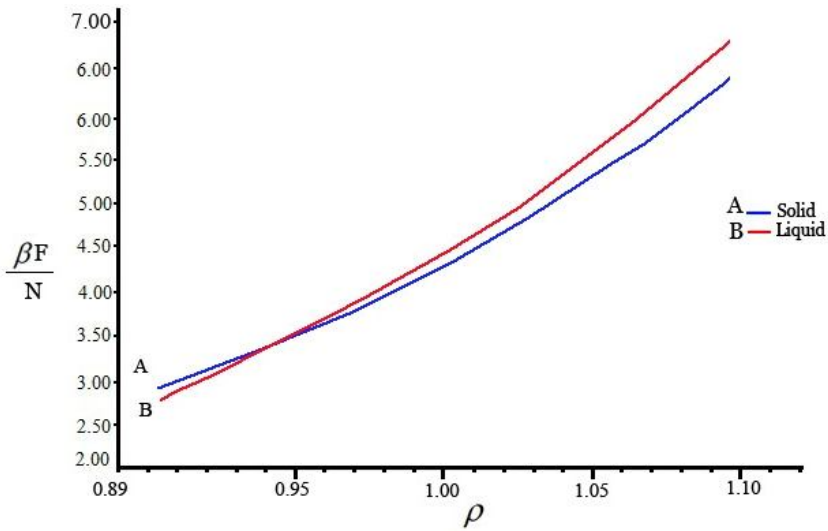

Fig. 4. The free energy of solid and liquid phase of polyethylene ($N = 6429$).

shown in Table 3, the difference between our result and McCoy's is about 10%, confirming the compatibility mapping to study the linear polymers.

Lindemann Criterion, Chemical Potential, and Solid and Liquid Phase Packing Fraction of Polyethylene

The chemical potential of polyethylene crystal ($N = 6429$) is obtained as bellow using packing fraction and diameter monomers $\sigma = 3/7\,A°$ [36]:

$$L = \sqrt{\frac{3}{\alpha a^2}} = 0.154 \qquad (31)$$

The rate of change of Lindemann criterion is a criterion for liquid-to-solid phase transition. The chemical potential and solid and liquid phase packing fraction were calculated by $\pi\rho_s/6$, $\pi\rho_l/6$, respectively [36].

Despite the high importance of these quantities for polyethylene ($N = 6429$), they have not been calculated yet. Therefore, we calculate them, though we cannot compare

Table 2. Comparison of Solid and Liquid Phase Dnsities of Polyethylene in the Transition Point of Different Methods.

Method	ρ_l	s
Experimental [56-58]	0.78	0.95
P-RISM [46]	0.77	1.13
MWDA (this work)	0.78	0.82

Table 3. Comparing the Results of Compressibility Factor of Polyethylene in Liquid Phase in Different Methods.

Method	β/K_T
McCoy [46]	0.70
MWDA (this work)	0.77

Table 4. The Results of Lindemann Criterion, Chemical Potential and Solid and Liquid Phase Packing Fraction of Polyethylene by MWDA Method

μ_s	$\pi\rho_s/6$	$\pi\rho_l/6$	L
6.083	0.43	0.40	0.154

our results of these quantities with other works (Table 4). But because Lindemann criterion, chemical potential and solid and liquid phase packing fraction of polyethylene are functions of density and we showed the accuracy of density in Table 2, so our results has been confirmed.

CONCLUSIONS

In this article we presented the formulation method of a density functional theory MWDA for linear polymers. Some

rational approximations have been used to connect MWDA method to linear polymer chain model. For example, regarding the fact that chain polymers are only crystallized when the Cohen's effect size would be long enough in comparison with the range of nuclear-solid interactions between monomers, so we can use the standard model of hard spheres for all of them. The connection plays a rather small role in the crystallization of linear polymer chain model and it is limited to a direct correlation function independent of temperature. Increasing the chain length increases the chance of knotting, and crystallization will be more simple, as the result the correlation function used in this research was calculated just for polyethylene with $N = 6429$. After running computer programs and conducting calculations based on MWDA, as explained, the results were compared with their corresponding valued obtained through famous P-RISM method and experiments (Figs. 3 and 4). As obviously seen in Table 2, our results are closer to experimental quantities, both in ρ_s and ρ_l values, and are more exact in comparison with the P-RISM method. The liquid phase density in MWDA method, which is equal to its experimental quantity, is closer to its real value, by 0.01, compared to that in the P-RISM method. Also, the crystal phase density is closer to real quantity, by 0.06, compared to that in MWDA method. As shown in Table 1, our results for the length of monomers in the curve fitting method used in this research, is completely in agreement with other methods and experimental results. Also, quantities such as Lindemann criterion, chemical potential and solid and liquid phase packing fraction have been calculated in Table 4. Regarding the fact that they are calculated based on ρ_s, ρ_l, we can insist on their accuracy. Accordingly, it has been verified that the method of density functional theory based on MWDA, used in this research, has the capability to correct the analytical results related to liquid-solid phase transition polymer linear chain model, remarkably.

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