

POLYMER PERCUS-YEVICK IDEAL CHAIN APPROXIMATION FOR THE LENNARD-JONES CHAIN FLUID

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The structure and thermodynamic properties of the freely jointed linear chain fluid with monomers interacting by the Lennard-Jones potential are studied using the polymer Percus-Yevick (PPY) ideal chain approximation. The theory is based on the Wertheim's multi-density integral-equation theory for associating fluids, appropriately modified to describe the polymer fluids. In the case of the chain system composed of 4, 8 and 16 monomeric units the PPY ideal chain approximation is found to yield good agreement with corresponding computer simulation results for the internal energy at the entire range of the density and temperature studied. For the longer chains composed of 50 and 100 segments the agreement becomes slightly worse, especially at low values of the density. Predictions of the theory for the structure properties are less satisfactory, i.e. theoretical results for the intermolecular average site-site distribution function of 16-mer fluid is only in semiquantitative agreement with Monte Carlo simulation results. It is expected, that the theory will be more accurate in predicting overall average distribution functions and for the fluid of shorter chain length.

1. Introduction

During the last decade several off-lattice models for the structure and thermodynamic properties of the polymeric fluids have been proposed. Most of theoretical descriptions developed recently are based on the extension of the integral equation techniques developed for the fluids of small interaction-site molecules. These include the polymer reference interaction site model (PRISM) theory (see Refs. [1,2] and references therein), polymer Born-Green-Yvon (PBGY) theory [3,4], a version of PY theory for a mixture of associating species that associate into polymer fluids [5], theory based on the Chandler-Silbey-Ladanyi PY approximation for the site-site fluid [6] and multidensity polymer PY (PPY) theory for associating fluids [7,8] appropriately modified to describe the polymer fluids [9,10,2,11,12].

However the majority of the applications of these theories are restricted to the case of the hard-sphere chain fluids. Although this model reflects the most characteristic features of the polymer fluids, i.e. excluded volume

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effects and effects of chain connectivity, it is still highly simplified due to the absence of attractive forces. The model, which in addition to the chain connectivity provides a realistic description for both repulsive and attractive interactions between the chain segments is the freely jointed Lennard-Jones chain (LJC) model.

The goal of the present paper is to study the structure and thermodynamic properties of the LJC fluid using the numerical solution of the PPY ideal chain approximation. The paper is organized as follows. In Section 2 we discuss the model and present the corresponding version of the PPY approximation together with the details of its numerical solution. Numerical results and their comparison with the corresponding computer simulation results are discussed in Section 3 and in Section 4 our conclusions are collected.

2. The model and PPY ideal chain approximation

Let us consider the system which consists of the freely jointed LJ monomer chains with fixed bond length L , chain length of m monomer units and number density of monomers ρ . All the nonbonded monomers, regardless of whether they belong to the same molecule or to the different chain molecules interact via the following pair potential

$$u(r) = 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right] \quad (2.1)$$

where ϵ is the potential well depth and σ is the distance at which the potential is equal zero.

The present model is studied using the PPY ideal chain approximation [7–9]. The approach is based on the multidensity integral equation theory for the associating fluids [7,8] appropriately modified to describe the chain polymer systems [9]. The derivation of the PPY ideal chain approximation for the hard-sphere linear chain fluid has been discussed earlier [9]. Its extension to the case of the LJ chains is straightforward and we shall therefore omit any details and present here only the final results, specified for the model at hand.

The theory consists of the Ornstein-Zernike (OZ) like integral equation

$$\hat{\mathbf{H}}(k) = \hat{\mathbf{C}}(k) + \hat{\mathbf{C}}(k)\boldsymbol{\sigma}\hat{\mathbf{H}}(k) \quad (2.2)$$

where $\hat{\mathbf{C}}(k)$, $\hat{\mathbf{H}}(k)$ and $\boldsymbol{\sigma}$ are the matrices defined by

$$\hat{\mathbf{C}}(k) = \begin{pmatrix} \hat{C}_{00}(k) & \hat{C}_{0A}(k) & \hat{C}_{0B}(k) \\ \hat{C}_{A0}(k) & \hat{C}_{AA}(k) & \hat{C}_{AB}(k) \\ \hat{C}_{B0}(k) & \hat{C}_{BA}(k) & \hat{C}_{BB}(k) \end{pmatrix},$$

$$\hat{\mathbf{H}}(k) = \begin{pmatrix} \hat{H}_{00}(k) & \hat{H}_{0A}(k) & \hat{H}_{0B}(k) \\ \hat{H}_{A0}(k) & \hat{H}_{AA}(k) & \hat{H}_{AB}(k) \\ \hat{H}_{B0}(k) & \hat{H}_{BA}(k) & \hat{H}_{BB}(k) \end{pmatrix},$$

$$\boldsymbol{\sigma} = \begin{pmatrix} \rho & \rho/m & \rho/m \\ \rho/m & 0 & \rho/m^2 \\ \rho/m & \rho/m^2 & 0 \end{pmatrix},$$

and PPY ideal chain approximation, relating the direct $C_{\alpha\beta}(r)$ and total $H_{\alpha\beta}(r)$ partial correlation functions

$$Y_{\alpha\beta}(r) = H_{\alpha\beta} + \delta_{\alpha 0}\delta_{\beta 0} - C_{\alpha\beta}(r) \quad (2.3)$$

where the partial cavity correlation functions are defined by

$$H_{\alpha\beta}(r) + \delta_{\alpha 0}\delta_{\beta 0} = e_R(r)Y_{\alpha\beta}(r) + (\delta_{\alpha A}\delta_{\beta B} + \delta_{\alpha B}\delta_{\beta A})\frac{m(m-1)}{4\pi L^2\rho}\delta(r-L) \quad (2.4)$$

Here $e_R(r) = \exp[-\beta u(r)]$, $\beta = 1/kT$, $\hat{H}_{\alpha\beta}(k)$ and $\hat{C}_{\alpha\beta}(k)$ are the Fourier transforms of the functions $H_{\alpha\beta}(r)$ and $C_{\alpha\beta}(r)$, respectively, and the lower indices α and β take the values 0, A, B and denote the bonding states of the corresponding particles [7–9]. Elimination of the cavity correlation functions $Y_{\alpha\beta}(r)$ between (2.3) and (2.4) yields

$$C_{\alpha\beta}(r) = f_R(r)Y_{\alpha\beta}(r) + (\delta_{\alpha A}\delta_{\beta B} + \delta_{\alpha B}\delta_{\beta A})\frac{m(m-1)}{4\pi L^2\rho}\delta(r-L) \quad (2.5)$$

where $f_R(r) = e_R(r) - 1$.

In the present version of the theory the equilibrium properties of the system is described via average overall $g(r)$ and intermolecular $g^{(inter)}(r)$ pair distribution functions, which are related to the partial correlation functions $H_{\alpha\beta}(r)$ by [7–9]

$$g(r) = \frac{1}{m^2} \sum_{ij=1}^m g_{ij}(r) = 1 + \sum_{\alpha\beta} H_{\alpha\beta}(r) \quad (2.6)$$

$$g^{(inter)}(r) = \frac{1}{m^2} \sum_{ij=1}^m g_{ij}^{(inter)}(r) = 1 + H_{00}(r) + 2H_{0A}(r) + 2H_{A0}(r) + 4H_{AA}(r) \quad (2.7)$$

where i and j denote the site species and take the values $1, \dots, m$, $g^{(inter)}(r)$ is the site-site distribution function between the sites i and j belonging to the different chains and $g_{ij}(r)$ is the overall particle-particle distribution function between the pair of monomers, regardless of whether they belong to the different chains or to the same chain. In eq. (2.7) the symmetry property of the model is used, due to which $H_{0A}(r) = H_{A0}(r)$ and $H_{AA}(r) = H_{BB}(r)$. One can also define the intramolecular distribution function $\omega(r)$ via the following relation [9]

$$\omega(r) = 4\pi r^2\rho [g(r) - g^{(inter)}(r)] \quad (2.8)$$

The set of the OZ equation (2.2) together with its closure conditions (2.5) form a closed set of equations to be solved. However direct application of the numerical methods of solution to this set of equations is not convenient. A form more appropriate for the numerical calculations follows from (2.2) and (2.5) written in terms of the correlation functions which remains finite when m approaching infinity. In addition it is necessary to eliminate the delta-function term in the closure (2.5) and perform the correspondent renormalization of the OZ equation (2.2). With this goal in mind

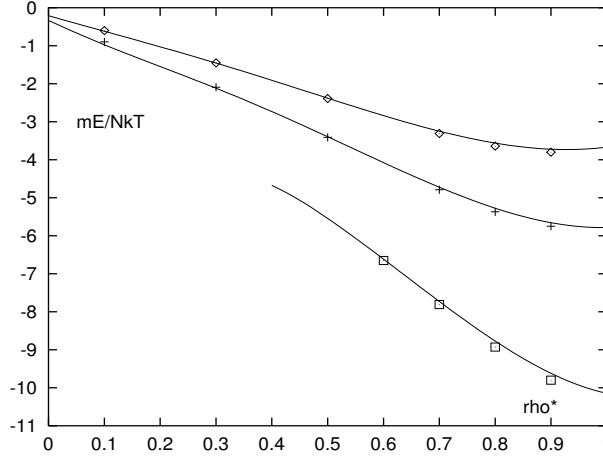


Figure 1. Internal energy mE/NkT of LJ 4-mers. Symbols are the MC results [13] for $T^* = 4, 3, 2$ from the top to the bottom, respectively. Solid lines are the present theory.

let us multiply both sides of the OZ equation (2.2) from the left and from the right by the matrix

$$\mathbf{X}_{\alpha\beta} = \delta_{\alpha\beta} \left[\delta_{\alpha 0} + (\delta_{\alpha A} + \delta_{\alpha B}) \frac{1}{m} \right] \quad (2.9)$$

which gives

$$\tilde{\mathbf{H}}(k) = \tilde{\mathbf{C}}(k) + \tilde{\mathbf{C}}(k) \boldsymbol{\rho} \tilde{\mathbf{H}}(k) \quad (2.10)$$

where $\tilde{\mathbf{H}}(k) = \mathbf{X} \hat{\mathbf{H}}(k) \mathbf{X}$, $\tilde{\mathbf{C}}(k) = \mathbf{X} \hat{\mathbf{C}}(k) \mathbf{X}$ and

$$\boldsymbol{\rho} = \begin{pmatrix} \rho & \rho & \rho \\ \rho & 0 & \rho \\ \rho & \rho & 0 \end{pmatrix}$$

The corresponding version of the closure conditions (2.4) and (2.5) take the form

$$\tilde{H}_{\alpha\beta}(r) + \delta_{\alpha 0} \delta_{\beta 0} = e_R(r) \tilde{Y}_{\alpha\beta}(r) + (\delta_{\alpha A} \delta_{\beta B} + \delta_{\alpha B} \delta_{\beta A}) \frac{m-1}{4\pi m L^2 \rho} \delta(r-L) \quad (2.11)$$

$$\tilde{C}_{\alpha\beta}(r) = f_R(r) \tilde{Y}_{\alpha\beta}(r) + (\delta_{\alpha A} \delta_{\beta B} + \delta_{\alpha B} \delta_{\beta A}) \frac{m-1}{4\pi m L^2 \rho} \delta(r-L) \quad (2.12)$$

To eliminate the delta-function term let us present these relations in the following form

$$\tilde{H}_{\alpha\beta}(r) = h_{\alpha\beta} + Q_{\alpha\beta}(r) \quad (2.13)$$

$$\tilde{C}_{\alpha\beta} = c_{\alpha\beta}(r) + \Delta_{\alpha\beta}(r) \quad (2.14)$$

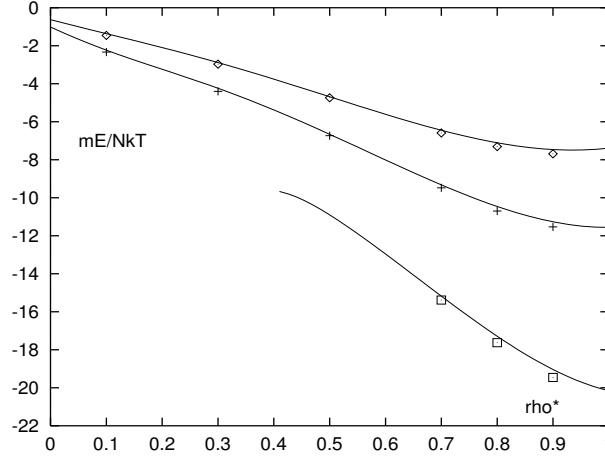


Figure 2. The same as in figure 1 for LJ 8-mers.

where

$$\Delta_{\alpha\beta}(r) = (\delta_{\alpha A}\delta_{\beta B} + \delta_{\alpha B}\delta_{\beta A}) \frac{m-1}{4\pi mL^2\rho} \delta(r-L)$$

and $Q_{\alpha\beta}(r)$ is defined such that, together with $\Delta_{\alpha\beta}(r)$ it satisfies the equation

$$\hat{\mathbf{Q}}(k) = \hat{\Delta}(k) + \hat{\Delta}(k)\rho\hat{\mathbf{Q}}(k) \quad (2.15)$$

where the matrices $\hat{\mathbf{Q}}(k)$ and $\hat{\Delta}(k)$ contain the elements which are the Fourier transforms of the elements $Q_{\alpha\beta}(r)$ and $\Delta_{\alpha\beta}(r)$, respectively.

Solution of this set of equations gives

$$\hat{Q}_{\alpha\beta}(k) = (\delta_{\alpha A}\delta_{\beta B} + \delta_{\alpha B}\delta_{\beta A}) \frac{m(m-1)\hat{s}(k)}{\rho(m^2 - \rho\hat{s}(k))} \quad (2.16)$$

where $\hat{s}(k) = \frac{\sin kL}{kL}$

Substituting Eqs. (2.13) and (2.14) into the OZ equation (2.10) and making use of equation (2.15) we obtain the OZ equation in the renormalized form

$$\hat{\mathbf{h}}(k) = \hat{\mathbf{S}}(k)\hat{\mathbf{c}}(k)\hat{\mathbf{S}}^T(k) + \hat{\mathbf{S}}(k)\hat{\mathbf{c}}(k)\rho\hat{\mathbf{h}}(k) \quad (2.17)$$

and corresponding closure relation

$$c_{\alpha\beta}(r) = f_R(r) [t_{\alpha\beta}(r) + \delta_{\alpha 0}\delta_{\beta 0} + (\delta_{\alpha A}\delta_{\beta B} + \delta_{\alpha B}\delta_{\beta A})] W(r) \quad (2.18)$$

where $\hat{\mathbf{S}}^T(k)$ is the matrix transposed to the matrix $\hat{\mathbf{S}}(k)$, $\hat{\mathbf{s}}(k) = \mathbf{1} + \hat{\mathbf{Q}}(k)\rho$, $t_{\alpha\beta}(r) = h_{\alpha\beta}(r) - c_{\alpha\beta}(r)$ and $W(r)$ is represented by its Fourier transform

$$\hat{W}(k) = \frac{m-1}{m} \frac{\hat{s}(k)}{m^2 - \rho\hat{s}(k)} \quad (2.19)$$

Now the initial set of equations is written in the form suitable for the numerical calculations. Solution of this set of equations is obtained using the method of direct iterations.

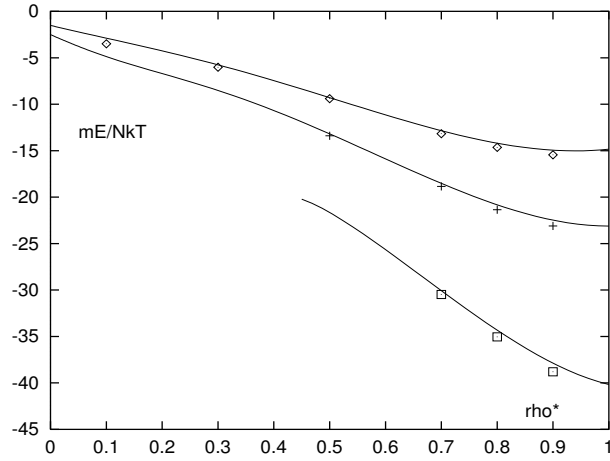


Figure 3. The same as in figure 1 for LJ 16-mers.

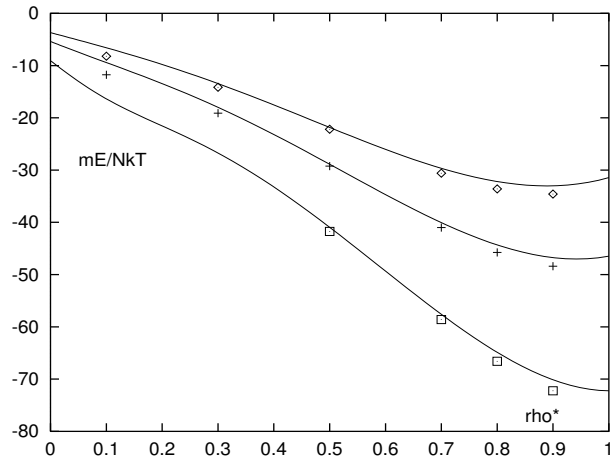


Figure 4. Internal energy mE/NkT of LJ 50-mers. Symbols are the MC results [13] for $T^* = 5, 4, 3$ from the top to the bottom, respectively. Solid lines are the present theory.

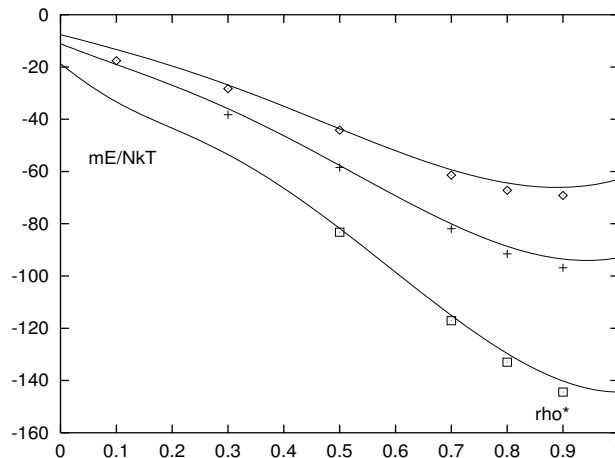


Figure 5. The same as in figure 4 for LJ 100-mers.

3. Results and discussion

The equilibrium properties of the model at hand are defined by the reduced density $\rho^* = \rho\sigma^3$, bonding length L , which is chosen to be $L = \sigma$, chain length m and reduced temperature $T^* = kT/\epsilon$. We will present first the results for the residual internal energy E , defined by the standard relation

$$\frac{E}{NkT} = 2\pi\rho \int_0^\infty r^2 u(r) g(r) dr. \quad (3.20)$$

where N is the number of monomers, i.e. $\rho = N/V$.

In figures 1-5 the results of the theory for the polymer systems with the chain length $m = 4, 8, 16, 50$ and 100 at different values of the temperature T^* and density ρ^* are compared with the corresponding Monte Carlo (MC) simulation results [13].

For relatively short chains ($m = 4, 8, 16$) the agreement is very good at all values of the temperature and density, while for the longer chains ($m = 50, 100$) the agreement becomes slightly worse, although it is still reasonably good. For the values of the density approaching zero the agreement between theory and simulation for longer chains ($m = 50, 100$) is not that good, although the theory properly predicts the nonzero value of E due to the intramolecular interactions.

Comparison of theoretical results and corresponding MC simulation results [14] for the intermolecular distribution function $g^{(inter)}(r)$ for 16-mers at three values of the density $\rho^* = 0.898, 0.5, 0.102$ and different values of the temperature $T^* = 8, 4, 2$ is demonstrated in figures 6 and 7.

In general the agreement here is only semiquantitative, although in the case of $\rho^* = 0.102$ and $T^* = 4$ the agreement becomes quantitative. For the sake of completeness on the same figures we show the overall pair distribution function $g(r)$. Unfortunately computer simulation results are not available for $g(r)$. As one would expect, with the decrease of the density the difference between $g(r)$ and $g^{(inter)}(r)$ increases. Similar, as in the case of the hard-sphere chain fluid [9], at $r = 2L$ $g(r)$ has jump discontinuity, which reflects the rigidity of bonding between the adjacent monomers. Finally in figure 8 we show the intramolecular distribution function $\omega(r)$ for 8-mers at

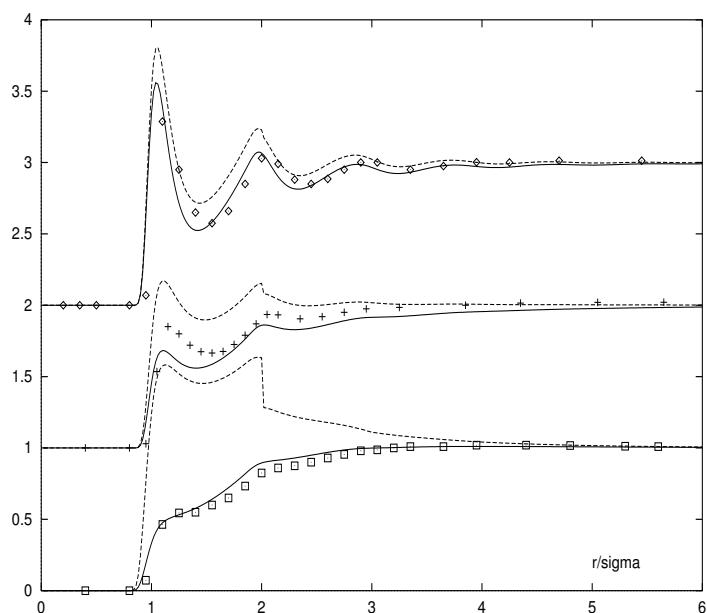


Figure 6. Average intermolecular distribution function $g^{(inter)}(r)$ from the present theory (solid lines), MC simulation (symbols) and average overall distribution function $g(r)$ from the present theory (dashed lines) for 16-mer LJ chains at $T^* = 2$; $\rho^* = 0.898$, $T^* = 2$; $\rho^* = 0.5$ and $T^* = 4$; $\rho = 0.102$ from the top to the bottom

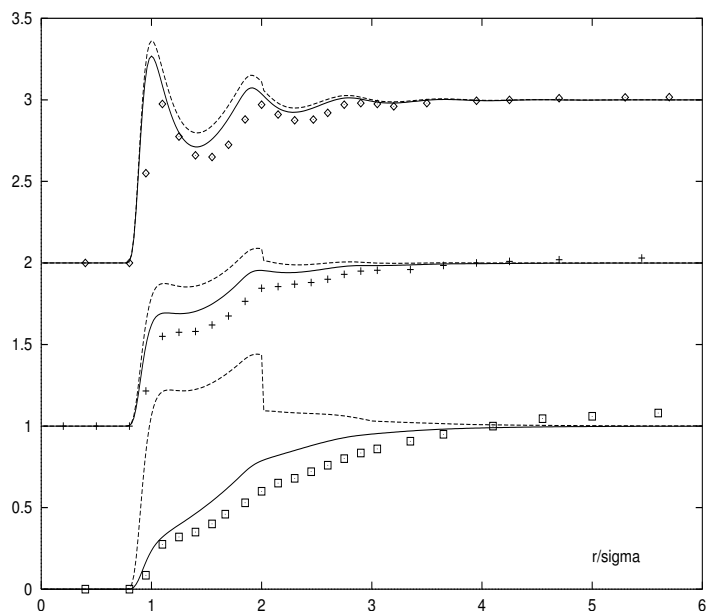


Figure 7. Average intermolecular distribution function $g^{(inter)}(r)$ from the present theory (solid lines), MC simulation (symbols) and average overall distribution function $g(r)$ from the present theory (dashed lines) for 16-mer LJ chains at $T^* = 8$ and $\rho^* = 0.898, 0.5, 0.102$ from the top to the bottom

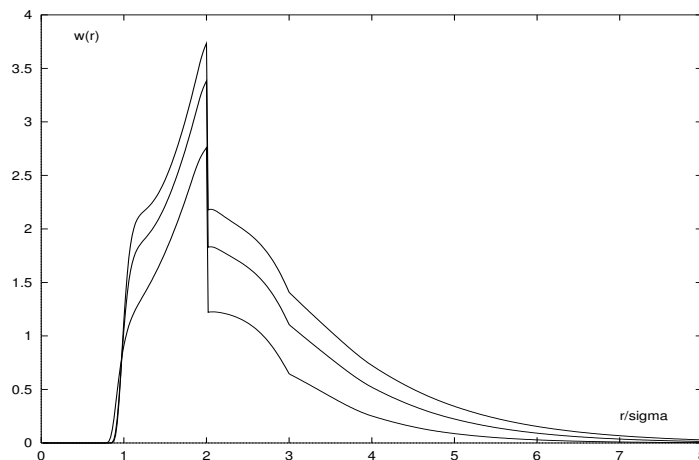


Figure 8. Average intramolecular distribution function $\omega(r)$ from the present theory at $T^* = 2.5, 3, 8$ from the top to the bottom.

different values of the temperature. Again, computer simulation results are not available here. Similar, as in the earlier studies [9] the intramolecular distribution function $\omega(r)$ obtained within PPY ideal chain approximation is not sensitive to the changes in the density, at $r = 2L$ it has a jump discontinuity and for $r > mL$ $\omega(r)$ is nonzero, although its value is relatively small there. The increase in temperature causes the overall decrease of $\omega(r)$.

4. Conclusions

In this paper the internal energy, average site-site intermolecular and particle-particle overall pair distribution functions of the fluid of freely jointed Lennard-Jones monomers are studied within the PPY ideal chain approximation. Theoretical predictions for the internal energy of the systems consisting of the chains of the length $m = 4, 8, 16, 50, 100$ are in good agreement with the corresponding computer simulation predictions. The structure properties are predicted less accurate, i.e. the results of the present approach for the intermolecular distribution functions of 16-mers are only in semiquantitative agreement with MC simulation results. The accuracy of the present theory for the structure properties has been assessed only in the case of 16-mer system, since computer simulation results are not available for the shorter chains. We would expect, on the basis of previous studies [9,10] and studies carried out here, that the PPY ideal chain approximation will be of higher accuracy for the overall pair distribution function and for the chains of shorter length, but this remains to be tested.

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**ЗАСТОСУВАННЯ ПОЛІМЕРНОГО НАБЛИЖЕННЯ
ПЕРКУСА-ЙЕВІКА ТА ІДЕАЛЬНОГО ЛАНЦЮГА ДЛЯ ОПИСУ
РІДИНИ ЛАНЦЮГОВИХ МОЛЕКУЛ З ВЗАЄМОДІЄЮ
ЛЕНАРДА-ДЖОНСА МІЖ СЕГМЕНТАМИ.**

Ю.В.Калюжний

За допомогою полімерного наближення Перкуса-Йевіка та наближення ідеального ланцюга досліджені рівноважні властивості рідини, що складається з ланцюгових молекул з потенціалом взаємодії Ленарда-Джонса між сегментами ланцюга. Теорія базується на багатогустинній теорії інтегральних рівнянь Вертхайма, відповідно узагальненій на випадок полімерних рідин. Виявлено, що у випадку системи, що складається з молекул, довжиною 4.8 або 16 мономерних одиниць, результати наближення добре узгоджуються з відповідними результатами комп'ютерної симуляції для внутрішньої енергії. Для ланцюгів довжиною 50 та 100 сегментів це узгодження дещо погіршується, особливо при малих густинах. Результати теорії для структурних властивостей є менш задовільні. У випадку системи, що складається з молекул довжиною 16 сегментів теоретична міжмолекулярна атом-атомна функція розподілу є лише в напівкількісній згоді з відповідними результатами комп'ютерної симуляції. Слід сподіватися, що теорія буде найбільш успішною у випадку повної атом-атомної функції розподілу та для молекул відносно короткої довжини.