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Additional Information

Conformation and dynamics of a diluted chain in the presence of an adsorbing wall. A simulation with Bond Fluctuation Model

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Abstract

Bond fluctuation model has been used to simulate the adsorption process of a single long polymer chain on an adsorbing surface. Simulations start at high temperature with the chain in an equilibrium coil structure. The inter- and intra chain energy potential were selected in such a way that on cooling the polymer chain vitrifies without any indication of chain ordering or chain folding. The structure attained on cooling is analyzed for a range of values of the interaction potential between the surface and the polymer segments. Adsorption is measured by the fraction of polymer segments situated on the adsorbing wall while crystalline ordering is characterized by the pair correlation function $g(r)$, the bond order parameter $P_2(r)$ and the bond correlation function $M(j)$. Isothermal adsorption is followed as well as a function of temperature. The work shows that adsorbing surface nucleates crystalline order by suppressing one dimension in the segmental mobility of the polymer chain.

Keywords: Bond Fluctuation Model, Polymer chain, Random coil, Adsorption process

1. Introduction

The physical properties of polymer chains in equilibrium are characterized by phase transitions, as the coil-globule transition of a single long chain in solution, the fluid-solid transition of the globule, or the adsorption transition of the chain at a wall [1-4]. The knowledge of these transitions and the conformation of the chain at the different states are still problems not fully understood. The adsorption of polymers on surfaces is an important phenomenon from the practical and theoretical point of view. In many industrial processes adsorbed polymers are used as glues or lubricants, and also it is an important issue in pharmaceutical applications [5], biophysics [6-8] and biological processes [9-12].

Phase transitions of single polymer chains in the bulk and in the presence of an adsorbing wall have been studied through model simulations [13-17]. In equilibrium states, the phase diagram as a function of temperature shows coil, liquid globule, solid globule, adsorbed coil (or adsorbed-extended) and adsorbed globule (or adsorbed compact) configurations, depending on the monomer wall attraction potential [13-15]. A drying or wetting adsorbed globule (or surfaced attached globule) with a nonzero contact angle has also been suggested [16].

It is well known that metastable polymer states play an important role in polymer physics. Depending not only, but mainly on temperature, the mobility of the polymer chain is some times so limited that an out of equilibrium conformation remains in time. That could be the case of experimental results on single chains in solution where the coil-globule transition has been measured [18] and results indicate the existence of (meta-)stable globular configuration [19]. In the bulk, this mobility restriction produces a glass transition and structural relaxation phenomena. In the glass transition temperature interval, the segmental mobility of the chains collapses and the polymer chains are frozen in an out of equilibrium state with severely limited (but not null) mobility. The system evolution towards equilibrium state at temperatures below the glass transition has been referred to as structural relaxation [20-23]. During this process, when maintaining temperature, pressure or other external condition, a decrease in volume, enthalpy, entropy or free energy can be observed.

In a previous paper [24] we have simulated using Bond Fluctuation Model (BFM) different conformations of a single long polymer chain. The interaction between non-bonded segments was governed by a Lennard-Jones potential. On the other hand, two energy potentials related to bond length and bond angle steered the intramolecular interactions. Varying the bond angle potential intensity, which tended to extend the polymer chain, we studied the changes in the chain configuration. Initially the system was subjected to a cooling ramp, followed by an isothermal annealing at different temperatures. Different conformations were found, such as amorphous globules or closed packed polymer strut nanophases.

In this paper we keep the potentials of the previous paper and present the results of the Monte Carlo simulations with the BFM model of a semiflexible polymer chain in the presence of an adsorbing wall. The influence of the wall-polymer interaction in the conformation of the chain was investigated. We studied the adsorption with different values for the wall potential and different thermal treatments. As we are interested in chain dynamics, the BFM [25] with the Metropolis criterion [13] is preferred over other methods as the Wang-Landau, which is more appropriate for equilibrium properties or phase transition studies [19, 26]. The main aim of this study is to analyze the behaviour of a semiflexible chain in a confined space and in presence of an adsorbing wall in order to obtain a deeper insight in the morphology of the system.

2. Simulations

The Bond Fluctuation Model (BFM) is a Monte Carlo simulation model in which each segment of the polymer chain (or effective monomeric unit) occupies the empty space forming a cube in a three-dimensional cubic lattice [27, 28]. The bond length between two consecutive monomeric groups in the chain can change from 2 to $\sqrt{10}$ lattice units. However, in order to avoid bond crossing, the distance $\sqrt{8}$ is not allowed.

The model dynamics consists of randomly choosing a monomeric group and one direction of movement. Taking into account if the volume exclusion is not violated and the new bond bonds are allowed, the movement can be performed with the probability obtained by the Metropolis criterion [27]:

$$P = \min \left[1, \exp \left(\frac{-\Delta E}{k_B T} \right) \right] \quad (1)$$

In this expression, ΔE is the increase of energy caused by the evaluated movement, k_B is Boltzmann's constant and $k_B T$ is proportional to the system temperature. The units of $k_B T$ are the arbitrary energy units and have also been used for potentials. The behaviour of the system can be determined by the ratio between energy and $k_B T$ in the exponent of the equation 1. Depending on the relationship with the interaction potentials a particular temperature can be considered as high or low.

We have employed three interaction potentials between the segments of the chain: a Lennard-Jones, a bond length and a bond angle potential. The intermolecular interaction between molecular groups in the system is governed by Lennard-Jones (LJ) potential, calculated for the non-bound monomers up to a distance of four lattice units [29]:

$$U_{LJ} = 4\varepsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right] \quad (2)$$

where σ is 2.0 lattice units, in order to be coherent with the excluded volume imposed by the lattice conditions of the model and ε is a parameter that regulates the intensity of the potential.

One of the intramolecular potential is the bond length potential [29]:

$$U(l) = U_0 (l - l_0)^2 \quad (3)$$

where the minimum energy distance is for $l_0=3$ lattice units and U_0 regulates the potential strength.

And finally, the second intramolecular potential is the bond angle potential [24, 30], where V_0 regulates the potential intensity, and the minimal energy angle θ_0 is assigned to 180° :

$$V(\theta) = V_0 (\cos \theta - \cos \theta_0)^2 \quad (4)$$

In the above-mentioned paper [24] we studied the configuration and the dynamics of a long chain diluted at low density in a BFM lattice and subjected to different thermal treatments. The final conformations of the chain were the result of the combination of inter and intramolecular interactions and the restrictions imposed by the segment packing of the chain in globule or coil conformation. The inclusion of the bond angle potential played an important role in the chain configuration. For the present simulation, we have chosen the parameters that showed a wide range of typologies for the chain, as condensed structures with co-continuous phase-separation (strut nanophases), as well as random coil or globular structures. The bond angle potential parameter has a considerably high value ($V_\theta=0.4$), boosting the stretching of the chain to conform this kind of co-continuous structures. The value of the bond length potential parameter ($U_\theta=0.45$) is 3 times higher than the Lennard-Jones potential parameter ($\epsilon=0.15$) and the sum of the 3 parameters is fixed as 1.

After we have studied the behaviour of a diluted single chain in a previous publication [24], the aim of this paper is to study the influence of the wall-chain interaction on the conformation of the chain when the wall-chain interaction potential is increased, keeping constant the inter and intramolecular potentials in the chain and only varying the wall-chain potential. The interaction potential between the chain and the wall has been considered as an intermolecular interaction, following the Lennard-Jones potential expression:

$$U_{LJ-wall} = 4\epsilon_w \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right] \quad (5)$$

where σ is 2.0 lattice units, to be coherent with the excluded volume imposed by the lattice conditions of the model used in the simulation. Five different chain-wall interaction parameter values were simulated, beginning with $\epsilon_w=0$ (without wall-chain interaction), and increasing the interaction parameter to 0.05, 0.10, 0.15 and 0.45.

The simulation lattice consists of a three-dimensional cubic box with side $L=100$ lattice units, and periodic boundary conditions on 2 of the 3 dimensions. This box is composed of two different parts. A wall is placed on one face of the non-periodic dimension of the simulation space. This wall is full of monomeric units characterized by a high intensity Lennard-Jones potential (equation 2) between them (ϵ parameter is 10^3), so the

monomeric units are joined together forming the crystalline wall. The wall occupies a surface of 100×100 lattice units and the thickness is 6 lattice units (this corresponds to 3 monomeric units or layers). This thickness was chosen taking into account that the Lennard-Jones potential was calculated up to a distance of four lattice units. On the other hand, a chain formed by 4000 monomeric units was randomly placed in the rest of the simulation box.

An initial equilibration period of 10^5 Monte Carlo Steps (MCS) at high temperature $k_B T = 5$ was performed in the system obtaining a random coil conformation of the chain. This initial period was followed by a fast cooling ramp at a constant rate of $-0.1 k_B T / 1000$ MCS until $k_B T = 2$, while the chain was still in equilibrium. After this, a second slower cooling ramp followed, at $-5 \cdot 10^{-5}$ units of temperature every 1000 MCS until $k_B T = 0.01$ in order to analyze the dynamics of the chain with slow changes in the system temperature.

Besides the thermal treatment indicated in the last paragraph, a different thermal treatment has been applied only to the system with the wall-chain attraction potential $\epsilon_w = 0.15$. After the same initial equilibration period (10^5 MCS) a fast cooling ramp at $-0.1 k_B T / 1000$ MCS was carried out until $k_B T = 0.01$. Different isothermals with 10^7 MCS were carried out at different temperatures from the states attained at the fast cooling ramp in order to study the out-of-equilibrium evolution of the system conformation when temperature remains constant. For the purpose of getting statistically independent data, all simulations in this study were performed for 10 different initial configurations.

The characterization of the system was performed using some measurable variables applied along the simulation process. The structural properties were studied by the pair correlation function [31] defined as:

$$g(r) = \frac{2L^3 H(r)}{(NP)^2 h(r)} \quad (6)$$

where $H(r)$ represents the histogram that counts the number of times that the allowed distance r occurs, L is the box simulation size, $h(r)$ is the number of possible r -vectors for a given distance r in the lattice and NP is the total number of particles.

To study the bonds orientation in the chain, two different functions were calculated. The first function was a bond parameter based on the 2nd Legendre polynomial of the scalar product [32] and defined as:

$$P_2(r) = \frac{1}{2} \langle 3(\bar{u}_i \cdot \bar{u}_j)^2 - 1 \rangle \quad (7)$$

with u_i and u_j being the normalised vectors corresponding to every pair of bonds i, j whose respective centres of mass are located at the distance r .

The second function obtained was the bond correlation function [33] that characterizes the stretching of the segments and obtained as:

$$M(j) = \langle \cos \theta_{i,i+j} \rangle \quad (8)$$

where $\theta_{i,i+j}$ is the angle between bonds i and $(i+j)$.

3. Results

The evolution of the mobility of the chain with temperature has been studied for the two different thermal treatments applied. The first thermal treatment performed was a slow cooling ramp ($-5 \cdot 10^{-5} k_B T / 1000 \text{MCS}$) from $k_B T = 2$ until $k_B T = 0.01$ carried out for different wall-chain interaction values indicated above. Figure 1 shows the number of molecular groups along the Z axis during the cooling ramp at different temperatures (worth noting that the wall was located between $Z=0$ and $Z=5$). If no interaction wall-chain potential is applied (Figure 1a), some changes in the configuration of the chain appear, but there are not any molecular groups adsorbed in the wall. As temperature decreases, the density at the center increases from the average density of around 40 chain groups per layer until 200 at $k_B T = 0.2$, showing the formation of a globule. The number of possible configurations of the chain is lower near the walls, making that states less probable. That entropic repulsion of the opposite faces of the non-periodic dimension Z of the simulation box is shown as a density reduction at $Z=6$ and 99 (Figure 1a). When increasing the wall-chain interaction potential, the molecular groups attached to the wall raise quickly, as can be seen in Figures 1b to 1d.

Figure 2 shows the snapshots diagram of the system at the end of the slow cooling ramp for different wall-chain interaction values. The plot shown in Figure 2a represents the system without interaction potential between the chain and the wall. In this situation the chain collapses in a globule far from the walls. When the interaction potential increases to $\epsilon_w=0.1$ (Figure 2b) and $\epsilon_w=0.15$ (Figure 2c), several molecular groups of the chain are adsorbed and crystallized while the molecular groups without contact with the wall conform a globule, which is totally amorphous as we will see below. The higher is the interaction potential, the closer to the wall is the globule, and more molecular groups are adsorbed. Finally, when the interaction potential increases to $\epsilon_w=0.45$, the chain is totally adsorbed showing a crystalline structure (Figure 2d).

With the aim of analyzing the dynamics of the system along this process, we have plotted in Figure 3 the pair correlation function $g(r)$ (eq. 6), choosing the configurations where we have found both globule and crystallization of the adsorbed groups, $\epsilon_w=0.10$ in Figure 3a and $\epsilon_w=0.15$ in Figure 3b. The function has been represented for two different temperatures in each plot. It can be seen that the value of the function increases when the temperature decreases, and at lower temperatures the function shows several peaks with a high value of the pair correlation. The value of the peaks increases when the wall-chain interaction potential does. Furthermore, Figure 4 shows the pair correlation function for the system with higher interaction potential ($\epsilon_w=0.45$), where the whole chain is adsorbed. The values found for the function follow the same trend as Figure 3, highlighting the high values obtained in the peaks for the lowest temperature.

In order to characterize the orientation of the bonds, the second order Legendre polynomial $P_2(r)$ (eq. 7) and the bond correlation function $M(j)$ (eq. 8) have been calculated. Figure 5 shows the second order Legendre polynomial results for $\epsilon_w=0.15$ at two different temperatures for distances greater than 5. At higher temperatures ($k_B T=0.5$) the average value of the function is around zero, however, when temperature decreases ($k_B T=0.14$), this average value increases, as may be noted in the solid line drawn in the figure.

The number of molecular groups at each layer of Z axis, and the second order Legendre polynomial for the interaction potential ($\epsilon_w=0.45$), have been plotted in Figure 6 at two different temperatures, $k_B T=1.25$ and $k_B T=0.25$. The number of adsorbed molecular

groups at the higher temperature (Figure 6a) is low (around 275) while for the lower temperatures this quantity has increased until around 2200 (Figure 6b). The second order Legendre polynomial function, $P_2(r)$, follows the same trend as the results shown in Figure 5; when the temperature decreases, the average value of the function increases from the null value shown in Figure 6a, to the value indicated by the solid line in Figure 6b.

To get further information about the bond orientation, specifically about the stretching between bonds, the bond correlation function, $M(j)$ (equation 8), has been represented for two different wall-chain interaction potentials, $\varepsilon_w=0.15$ and $\varepsilon_w=0.45$, at different temperatures (Figure 7). In both situations, at the higher temperature ($k_B T=1$) the values remain positive in a broad range, however, at the lower temperature ($k_B T=0.2$), the values change from positive to negative with a significant value both in positive and negative results. This change between positives and negatives values is related to folds in the chain, as can be seen in the inset of Figure 7a, where a sketch shows the values of the function for 4 segments in the chain with different angles between them (parallel, perpendicular and antiparallel configuration).

A second thermal treatment was applied only to the system with the wall-chain interaction potential $\varepsilon_w=0.15$, the same as the chain ε value. After the initial equilibration period at $k_B T=5$, a fast cooling ramp ($-0.1 k_B T / 1000$ MCS) was carried out, followed by isothermal simulations at different temperatures from states on the ramp. The adsorbed groups (at $Z=6$) at the beginning and at the end of the isothermals performed at different temperatures have been plotted in Figure 8. At the beginning of the isothermal simulations there are few molecular groups adsorbed in the wall, increasing slightly, as temperature decreases, along the cooling ramp. Along the isothermal treatments performed at several temperatures, the behaviour of the system shows a completely different behaviour. At temperatures from $k_B T=0.5$ to 0.2 , the number of molecular groups adsorbed during the isotherm increases with decreasing temperature. However for values lower than $k_B T=0.2$, the number of adsorbed molecular groups at the end of the isotherm decreases when temperature does. The isothermal simulations performed at temperatures lower than $k_B T=0.08$ show that the number of molecular groups adsorbed along the isotherm is nearly null.

Figure 9 shows the snapshots diagram of the chain in different situations during this second thermal treatment at the end of the isothermal periods, where the most representative conformations can be observed. At higher temperatures, $k_B T=0.35$ and $k_B T=0.3$, the conformation is a partially adsorbed random coil (Figure 9a and 9b) and when the temperature decreases, the conformation becomes a set of connected globules and crystalline segments adsorbed in the wall (Figure 9c). Finally, at $k_B T=0.1$ (Figure 9d), the chain shows a packed strut nanophase structure. The study of the dynamics of the system has been performed by means of the pair correlation function and the Second order Legendre polynomial function (Figure 10) at some of the temperatures shown in Figure 9. At the highest temperature ($k_B T=0.35$ in Figure 10a), the average value for the second order Legendre polynomial, $P_2(r)$, for distances > 2 is around zero. At $k_B T=0.18$ (Figure 10b), the function shows an average value higher than zero for a broad range of r and finally, at the lowest plotted temperature ($k_B T=0.1$ in Figure 10c), the function shows higher values for $r<10$ and remains close to zero for $r>10$. The pair correlation function for the same temperatures is shown in the insets of Figure 10. The results display that at $k_B T=0.35$ (inset of Figure 10a) there is a broad interval (around $r=40$) with significant values. For $k_B T=0.18$ (inset of Figure 10b), this interval becomes narrower (around $r=20$) while increasing the values, and at $k_B T=0.1$ (inset of Figure 10c), the interval where the number of times that the allowed distance r occurs, has significant values for distances between 0 and 15, and also high values for very short distances.

4. Discussion

The wall-chain interaction potential is the parameter that governs the adsorption process in the simulated system. If there is not wall-chain interaction potential, the conformation of the chain along the cooling ramp remains as a coil. The structure of the chain begins as a random coil filling the space of the simulation box and avoiding contact with both walls at $Z=6$ and 99 due to the entropic repulsion, as can be seen in the inset of figure 2a. When the slow cooling ramp is applied, the chain configuration starts to compact as temperature decreases, becoming a totally amorphous globule. The chain compacts around the centre of the simulation box, without any approach to the wall, as shown in Figure 1a. The adsorption process takes place when the wall-chain interaction potential is applied. Along the cooling ramp (from $k_B T=0.2$ to 0.01), the chain, with high

mobility at high temperatures, approaches to the wall and the molecular groups are adsorbed. The number of adsorbed molecular groups increases as the wall-chain potential does, as may be noted in Figures 1b, 1c and 1d. At $k_B T=0.75$, only the system with $\epsilon_w=0.45$ shows adsorbed molecular groups (results not shown). The different configurations obtained at the end of the slow cooling ramp are plotted in Figure 2, where only with the simulation with the highest value of the wall-chain interaction potential show the chain totally adsorbed ($\epsilon_w=0.45$ at $k_B T=0.01$). In the simulation performed for wall-chain interaction potentials lower than 0.45 (Fig. 2b with $\epsilon_w=0.1$ and Fig. 2c with $\epsilon_w=0.15$), the chain configuration displays a mixed structure between the globule for no wall-chain interaction structure (Figure 2a) and the totally adsorbed chain (Figure 2d). The molecular groups which reach the wall crystallize, nevertheless the rest of the chain remains amorphous, forming a globular structure.

The changes in the system along the cooling ramp have been studied by the evolution of the structural parameters. One of the function used is the pair correlation function $g(r)$ (equation 6), related to the probability of finding a monomeric unit at a given distance from a given another one, providing information about the packing of the chain. The conformation of the bonds has been analyzed using the Legendre function, $P_2(r)$, (equation 7) and the bond correlation function $M(j)$ (equation 8). The former provides information about the orientation between the bonds located at the same distance, r , and the latter allows us to study the orientation (angle) between bonds of the chain. In Figure 3a the pair correlation function $g(r)$ for the wall-chain potential $\epsilon_w=0.1$ at two different temperatures shows the presence of globular structures (indicated by the circle in the figure) with a distance in the lattice around 20 units (both at $k_B T=0.25$ and $k_B T=0.16$), at higher distances the function is close to zero. The function increases its value with decreasing temperatures, i.e. becomes a more compacted globule when the temperature decreases. The presence of peaks at the lower temperature isotherm indicates the possibility of preferred distances in the packing structure (see the arrows in the figure at $k_B T=0.16$) and it can be related to a crystallization process; however only the study of the bonds orientation can confirm this fact. A similar behaviour has been found for the wall-chain interaction $\epsilon_w=0.15$ (Figure 3b). This system evolves from a coil at high temperatures ($k_B T=0.4$), where the pair correlation function has very low values, to a more compacted globule as temperature decreases (the circle in the figure shows the function with significant values for distances r lower than 25 lattice units at

$k_B T=0.2$). Comparing this behaviour with those observed in the previous system ($\epsilon_w=0.1$), the results show more peaks, some of them with higher values, which could indicate a higher crystallinity degree. At the highest wall-chain interaction studied ($\epsilon_w=0.45$), the system does not show the presence of globular structures (Figure 4). At high temperature only a small packed structure can be seen in this system (shown in the inset of Figure 4 with more detail), i.e. the value of the pair correlation function is significant for distances lower than 10 lattice units (see the circle in the inset). Nevertheless, the packing does not change at lower temperature, but the presence of very high value peaks (indicated by the arrows) is related to the crystallized structure found at the end of the cooling ramp (Figure 2); this point will be further discussed below, when the bond conformation will be analyzed.

In order to analyze the crystallization process and its relationship with the presence of peaks in the pair correlation function $g(r)$, the bond order parameter $P_2(r)$ and the bond correlation function $M(j)$ have been obtained for all wall-chain interaction potentials at different temperatures along the cooling ramp. Figures 5 to 7 show the results obtained for the system with $\epsilon_w=0.15$ and 0.45 , where the possibility of crystallization is higher. In both cases, at high temperature there are molecular groups adsorbed (133 molecular groups for $k_B T=0.5$ in the system with $\epsilon_w=0.15$ and 275 molecular groups for $k_B T=1.25$ in $\epsilon_w=0.45$); however the chain does not show correlation between bonds (Figures 5 and 6a), and the bond correlation function $M(j)$ obtained for both systems remains positive (with values around zero) for a large interval. This fact can be seen in Figure 7 where high temperature ($k_B T=1$) has been represented ($\epsilon_w=0.15$ in Figure 7a and $\epsilon_w=0.45$ in Figure 7b) for the function. This behaviour is associated with a lack of correlation between the segments of the chain, so the chain remains amorphous, without any order in the configuration of the chain, both in the adsorbed groups and not adsorbed remaining molecular groups. When temperature decreases, correlation in long distances appears, as can be seen in Figures 5 and 6b, where the average value of the function $P_2(r)$ is higher than zero (solid line shows the average value). Furthermore, the chain presents a folded configuration, as shown in Figure 7, where at lower temperature ($k_B T=0.2$) the bond correlation function changes from a parallel to an antiparallel configuration (positive to negative values). For the wall-chain interaction potential $\epsilon_w=0.15$, the chain folds every 6 segments (Figure 7a), however when the wall-chain interaction increases ($\epsilon_w=0.45$ in Figure 7b), the chain folds every 4 segments. This is an

evidence of a more compact folding in the adsorbed chain when interaction wall-chain raises, as it is shown in the snapshot diagram plotted in Figure 2, where the presence of ordered structures related to the crystallized structure is more compacted when higher is the wall-chain interaction potential.

In short, the changes in the configuration of the chain depending on the wall-chain interaction potential involve the whole chain, which moves to the wall as the temperature decreases. As higher is the wall-chain interaction, more molecular groups are adsorbed in the wall. After the adsorption process, local motions produce the rearrange of the segments minimizing the energy of the system, so these segments crystallize. In the rest of the chain that is not adsorbed, the system evolution to a minimum energy state does not produce any kind of crystallization, but generates condensed globules with amorphous structure.

For the purpose of analyzing the evolution of the chain configuration during isothermal annealing, we have studied the system with wall-chain interaction potential $\epsilon_w=0.15$ applying a fast cooling ramp ($-0.1 k_B T/1000$ MCS) followed by an annealing process (10^7 MCS) at different temperatures. This system shows an interesting behaviour with both globular structure and crystallization reached at the end of the initial cooling ramp (Figure 2c); besides the ϵ of the chain equals ϵ_w , so when the chain is adsorbed, we can consider the process as a homogeneous crystal growing from the wall. The results obtained in this second simulation show that the number of adsorbed molecular groups during the fast cooling ramp increases slightly when temperature decreases due to the interaction potential between the wall and the chain, which attracts the chain to the wall. Nevertheless, important changes in the configuration of the chain are produced during the performed isothermal treatment (Figure 8). When the temperature is over $k_B T=0.2$, the number of molecular groups adsorbed along the annealing increases, but at temperatures lower than $k_B T=0.2$, the behaviour is the opposite. The glass transition temperature (T_g) obtained in the system as the intersection of extrapolated glass and liquid lines in the energy-temperature diagram (not shown) is $k_B T=0.18$, and this fact allows us to explain the change in the behaviour shown in Figure 8. At temperatures over the T_g , the chain evolves by means of cooperative conformational rearrangements that facilitate the adsorption process. Nevertheless, at temperatures below T_g , just local movements are allowed. Only molecular groups that are close enough to the wall can be

adsorbed because of local motions. At temperatures lower than $k_B T=0.13$ the chain remains almost frozen and only a few molecular groups are adsorbed in the annealing.

The most representative configurations found in the analysis of isotherms are shown in Figure 9. At the end of the isotherm performed at $k_B T=0.35$ (Figure 9a) molecular groups adsorbed to the wall can be found and the rest of the chain remains as a coil, showing a totally amorphous structure. When the annealing temperature drops at $k_B T=0.3$, the adsorbed molecular groups show a slight order in their configuration with a more stretched segment configuration along the wall. The rest of the chain (not adsorbed) remains in a random coil configuration with a tendency to pack in a globule (Figure 9b). When decreasing the annealing temperature, the chain shows a meaningful change in its configuration. At $k_B T=0.18$ (Figure 9c), the adsorbed chain shows an ordered structure while the not adsorbed chain shows a condensed globule configuration. Finally, at $k_B T=0.1$ (Figure 9d), the chain does not reach the wall (only a very few molecular groups are adsorbed) and the chain consists mostly in open aggregates of close packed segments (packed strut nanophases) with slight orientation in the packed segments (a similar configuration was found in [24]).

The pair correlation function $g(r)$ plotted in Figure 10 shows the presence of globules for the isotherms performed at $k_B T=0.18$ and 0.1 (inset of Figures 10b and 10c), however at the end of the annealing performed at $k_B T=0.35$ (inset of Figure 10a) the conformation of the chain does not show any globular configuration. The bond order parameter $P_2(r)$ remains around zero at $k_B T=0.35$ for distances > 3 (Figure 10a), which means that the chain does not show any kind of correlation in orientation, i.e., its configuration remains as a random coil for both adsorbed and not adsorbed molecular groups. When decreasing temperature, the chain displays a different behaviour associated with the presence of globular structures. At $k_B T=0.18$, the pair correlation function indicates the presence of globules (with a diameter around 20 lattice units) and the Legendre function shows a correlation in bonds for long distances and also an increase in the value for distances between 20 and 40 (Figure 10b). This result is related to the presence of the crystalline segments in the adsorbed chain at these distances; the crystalline structure shown by the adsorbed chain is also confirmed by the peaks (preferred distances) shown in the pair correlation function $g(r)$ (inset of Figure 10b). If the temperature decreases until $k_B T=0.1$, the pair correlation function (inset of Figure

10c) shows the presence of small globules (diameter around 12 lattice units) and the Legendre function $P_2(r)$ means the existence of a slight correlation between bonds at distances $r < 10$ with no peak that suggest the presence of crystallization. However the bond correlation function $M(j)$ (results not shown) does not indicate any correlation between near angles in the chain segments. This behaviour agrees with the open configuration shown in Figure 9d, where the chain shows a packed strut nanophase structure [24].

It is worth to be noted that the formation of a crystal in the model is given by the combination of several factors. First of all, the existence of the wall acts as a nucleus for the crystallization process. The loss of one degree of freedom in movements helps the system to find ordered configurations. Secondly, the Lennard-Jones potential helps the molecule to get close to the wall and stay packed and finally, the bond length and bond angle potentials help the packed chain to conform aligned structures on the regular surface given by the wall. The contribution of all these factors explains the

5. Conclusions

Monte Carlo models allow a coarse grained simulation of the different structures of a long polymer chain. With the inter- and intra-chain potential parameters used in this work cooling from a high temperature state in which polymer chains adopt an equilibrium coil conformation yields an amorphous glass, the glass transition taking place around $k_B T = 0.18$. The presence of an adsorbing surface in the proximity of the coil produces different structures depending on wall-chain interaction values and the applied thermal history. During a cooling ramp there are two competing processes, adsorption of the chain segments on the surface and vitrification of the non-absorbed parts of the chain. The parts of the chains that adsorb on the surface organize in more or less ordered crystalline structures, with chain folding characteristic of polymer crystallization. These structures were detected in the computer simulation by the pair correlation function $g(r)$, the Legendre function $P_2(r)$ and the bond correlation function $M(j)$ that proves chain extension and chain folding. Thus the attracting surface nucleates the formation of polymer crystals by eliminating one dimension to chain mobility. The parts of the chain that are not adsorbed form glassy globules whose size and shape depend on the simulation conditions. Isothermal adsorption reveals the role of temperature on the adsorption kinetics and crystalline ordering on the surface.

Obviously at temperatures below the glass transition, frozen chain mobility does not allow adsorption on the wall. The fraction of chain segments adsorbed on the surface attains its maximum just above the glass transition and then decreases with increasing temperature. Crystalline order on the wall follows the same characteristics found after slow cooling.

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Fig. 1. Molecular groups in Z axis along the cooling ramp performed at $-5 \cdot 10^{-5} k_B T / 1000$ MCS. a) $\epsilon_w=0$, $k_B T=0.4$ (full symbol), $k_B T=0.3$ (grey symbol), $k_B T=0.2$ (open symbol). b) $\epsilon_{\text{int}}=0.1$, $k_B T=0.75$ (full symbol), $k_B T=0.4$ (grey symbol), $k_B T=0.3$ (open symbol). c) $\epsilon_{\text{int}}=0.15$, $k_B T=0.75$ (full symbol), $k_B T=0.5$ (grey symbol), $k_B T=0.4$ (open symbol). d) $\epsilon_{\text{int}}=0.45$, $k_B T=1.75$ (full symbol), $k_B T=1.5$ (grey symbol), $k_B T=0.75$ (open symbol).

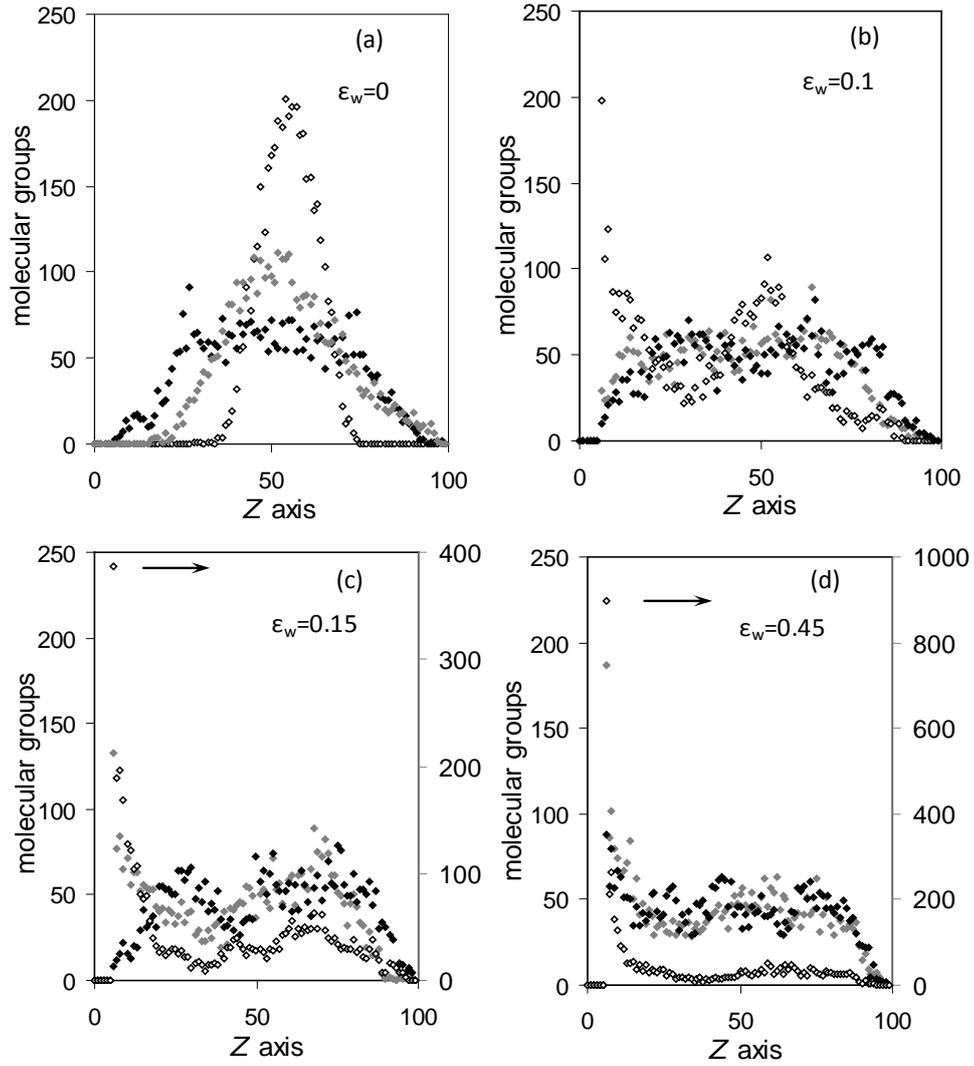


Fig. 2. Snapshots of the simulated system showing the chain and the end of the cooling ramp ($k_B T = 0.01$) at $-5 \cdot 10^{-5} k_B T / 1000$ MCS for different interaction wall-chain potential ε_w . a) $\varepsilon_w = 0$, b) $\varepsilon_w = 0.10$, c) $\varepsilon_w = 0.15$ and d) $\varepsilon_w = 0.45$. The inset in plot (a) shows the configuration of the chain at the end of the equilibration period.

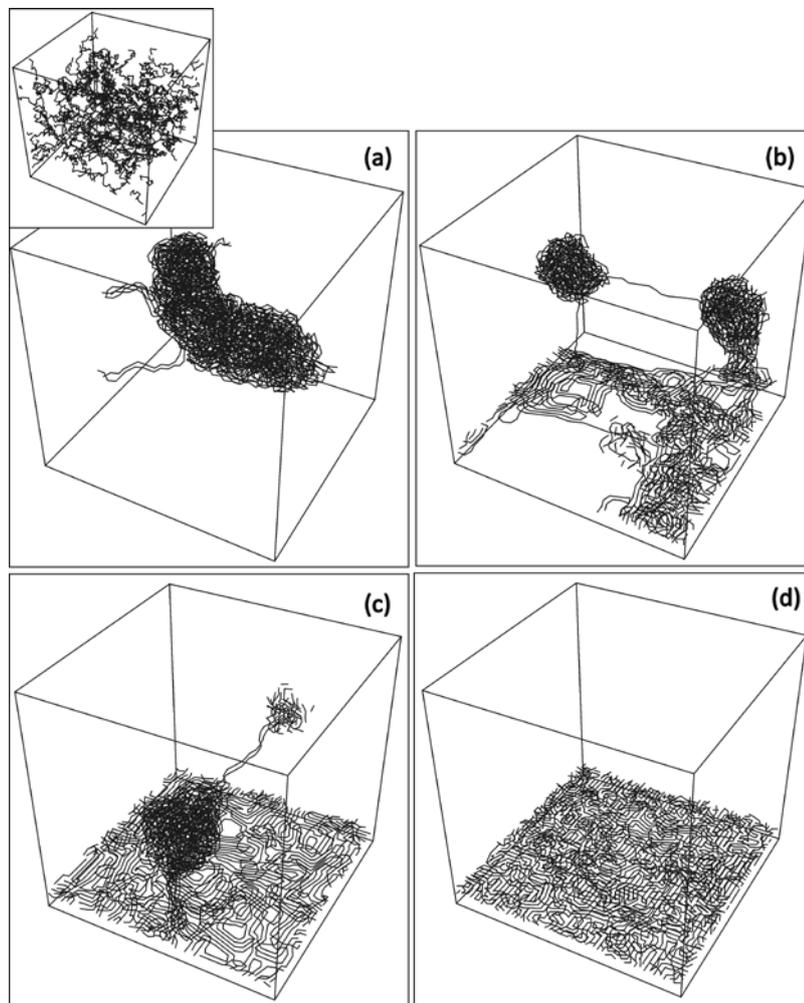


Fig 3. Pair correlation function $g(r)$ vs the distance measured in lattice units for two different interaction wall-chain potential along the cooling ramp at $-5 \cdot 10^{-5} k_B T / 1000$ MCS. a) $\epsilon_w=0.1$: $k_B T=0.25$ (black), $k_B T=0.16$ (gray). b) $\epsilon_w=0.15$: $k_B T=0.4$ (black), $k_B T=0.2$ (gray).

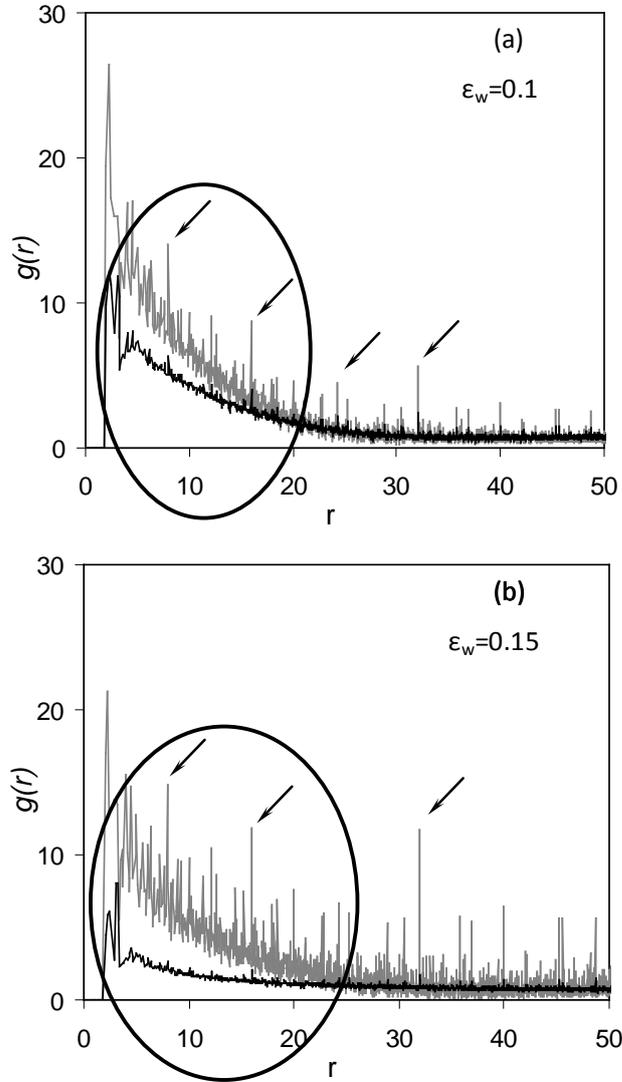


Fig. 4. Pair correlation function $g(r)$ vs the distance measured in lattice units for interaction wall-chain potential $\varepsilon_w=0.45$ along the cooling ramp at $-5 \cdot 10^{-5} k_B T / 1000$ MCS. $k_B T=1$ (black), $k_B T=0.25$ (gray). The inset shows the pair correlation function with more detail.

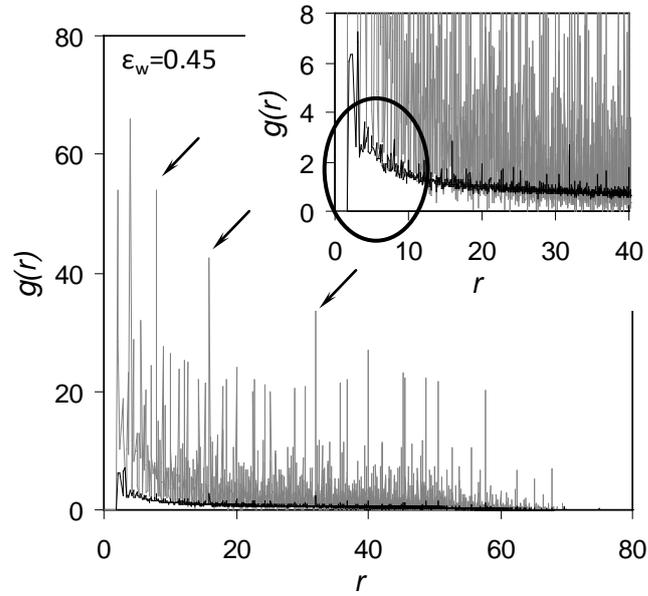


Fig. 5. Second order Legendre polynomial for interaction wall-chain potential $\varepsilon_w=0.15$ along the cooling ramp at $-5 \cdot 10^{-5} k_B T / 1000$ MCS. Open symbol for $k_B T=0.5$ and full symbols for $k_B T=0.14$. The solid line in the full symbol plot is a guide to the eye.

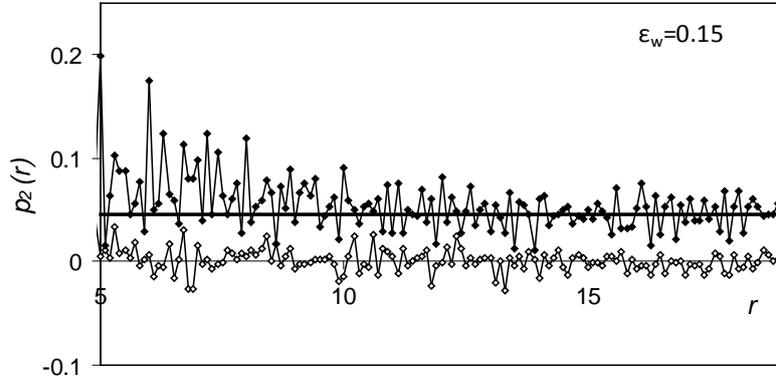


Fig. 6. Second order Legendre polynomial (open symbols) and molecular groups in Z axis (full symbol) for interaction wall-chain potential $\epsilon_w=0.45$ along the cooling ramp at $-5 \cdot 10^{-5} k_B T / 1000$ MCS. a) $k_B T=1.25$. b) $k_B T=0.25$. The solid line in plot (b) is a guide to the eye.

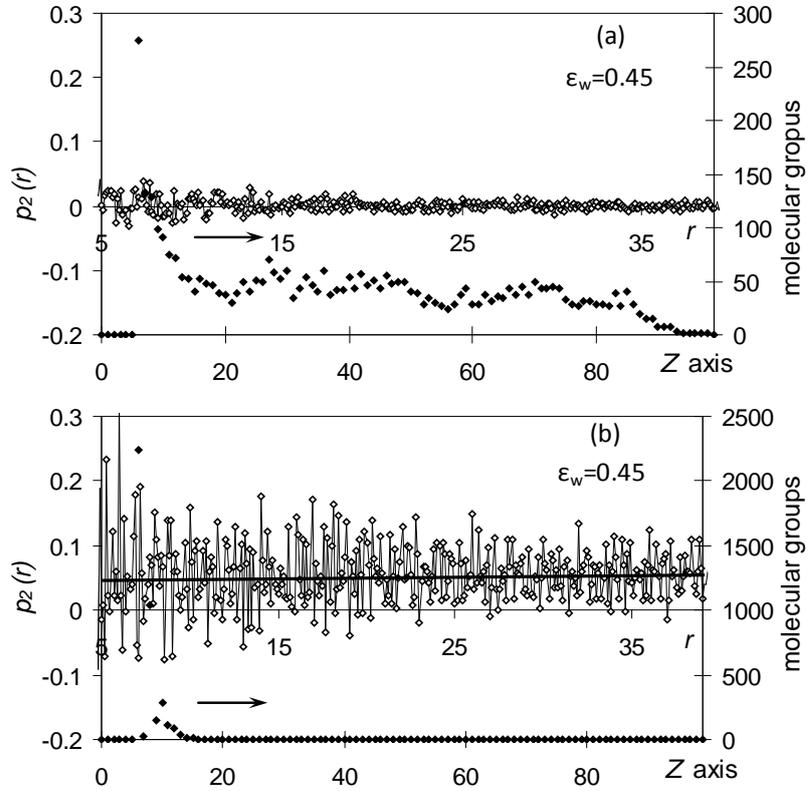


Fig. 7. Bond correlation function for interaction wall-chain potential $\varepsilon_w=0.15$ (plot a) and $\varepsilon_w=0.45$ (plot b) along the cooling ramp at $-5 \cdot 10^{-5} k_B T / 1000$ MCS. Full symbols for $k_B T=1$ and open symbols for $k_B T=0.2$. The inset shows the value of bond correlation function between different possible bond configurations.

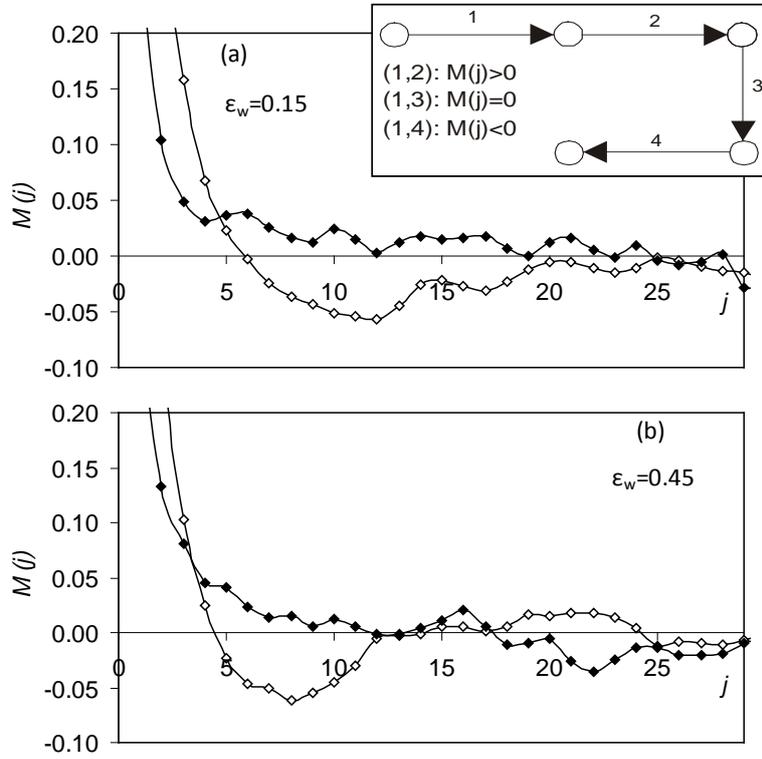


Fig. 8. Molecular groups in $Z=6$ at the beginning (open symbols) and end (full symbols) of the isotherms performed at different temperatures for wall-chain interaction potential $\epsilon_w=0.15$

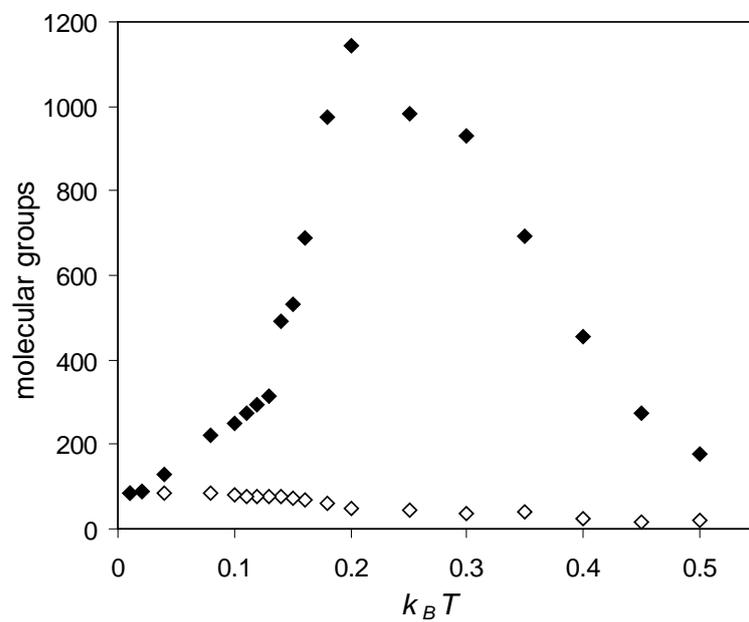


Fig. 9. Snapshots of the simulated system showing the chain at the end of isotherms at different temperatures for interaction wall-chain potential $\epsilon_w=0.15$. a) $k_B T=0.35$, b) $k_B T=0.30$, c) $k_B T=0.18$, d) $k_B T=0.1$

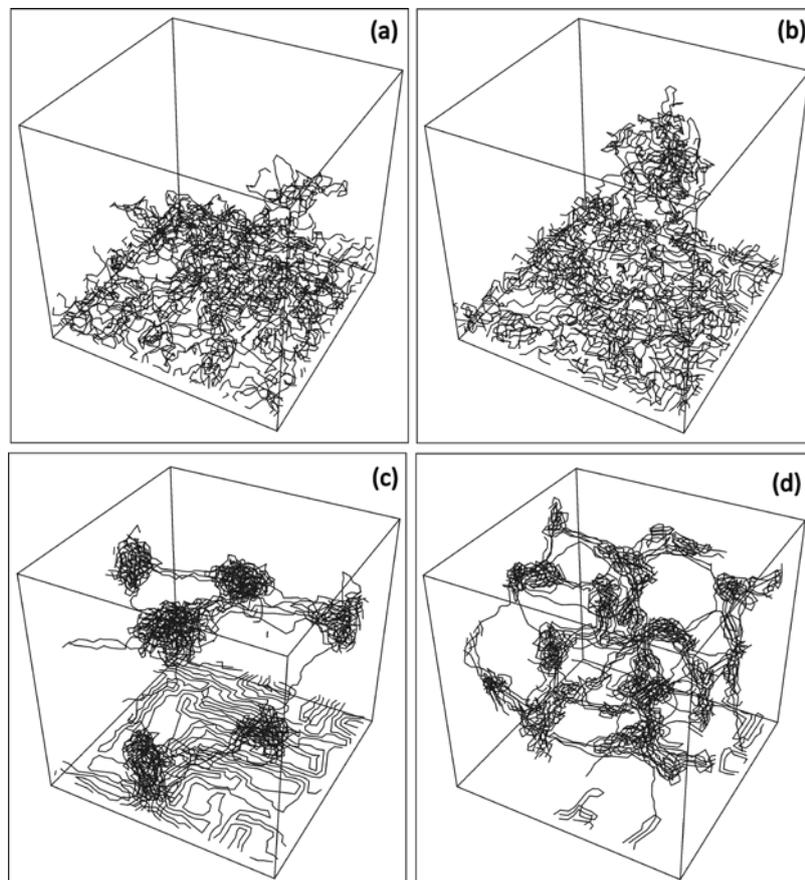


Fig. 10. Second order Legendre polynomial $P_2(r)$ vs the distance measured in lattice units for interaction wall-chain potential $\varepsilon_w=0.15$ at the end of the isotherms at different temperatures. a) $k_B T=0.35$. b) $k_B T=0.18$. c) $k_B T=0.1$. The insets show the pair correlation function $g(r)$ vs the distance measured in lattice units at the same temperature.

