# Simulation of Polymer Crystallization through a Dynamic Monte Carlo Lattice Model

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ABSTRACT: A simulation approach to polymer crystallization is presented. The molecules approach crystallization through a compact globule state. The simulation shows that individual molecules acquire a lamellar conformation, even before interacting to form a crystal. The lamellar thickness is considerably smaller than in the most stable state, in agreement with the experimental observations. The lamellar thickness is observed to decrease as a function of the temperature of simulation, also in agreement with the experimental observations.

## Introduction

Since the discovery that polymers crystallize as thin lamellae, a considerable amount of work has been carried out to understand the details and mechanism of crystallization. Excellent reviews can be found in two recent textbooks.[1,2] However, many features of polymer crystallization have been the subject of discussions which have not yet been settled. As stated by Strobl,[1] "simple solutions do not exist". Gedde states[2] that "perhaps a new paradigm for polymer crystallization will take shape in the coming years". The thickness of the obtained polymer crystals depends on the temperature of crystallization as it decreases at lower temperatures. This phenomenon is not well understood as, though this phenomenon seems kinetically governed, thermodynamic features contribute to the overall behavior.

Most models of polymer crystallization attempt to describe the process as a transition from a random coil molecule (dissolved or melted) onto the surface of a growing crystal. However, crystallization proceeds under conditions in which the dissolved or melted molecules are no longer in the random coil state; they should be in the form of collapsed globules, since crystallization proceeds at temperatures well below the melting or dissolution point. The coil−globule transition has been studied in great detail for its relevance to protein folding, as reviewed by Ptitsyn.[3] The collapse of amorphous polymers in poor solvents has also been studied in detail, a process which has also been recently reviewed.[4] However no consideration has been given to the fact that the collapsed molecule may crystallize. This possibility has been discussed by one of us in a recent review.[5] To our knowledge, only a preliminary account of this possibility has appeared in the literature.[6]

Though different in many aspects from heteropolymers, homopolymer chains are governed in their collapse to compact states and crystallization in poor solvents by rules in some respect similar to those which govern the acquirement of the unique native state of a protein although homopolymers have largely degenerate low energy states. Some of us recently proposed[7] a new algorithm, named the contact interaction (CI) method, for the conformational search of protein chains modeled as copolymers of hydrophobic and polar monomers configured as self-avoiding walks on square or cubic lattices. It proved largely superior to the standard Monte Carlo algorithm in the exploration of the low-energy regions of the conformational space and allowed us to run dynamic simulations in quite shorter times.

Other authors have studied collapsed homopolymer models on a square lattice,[8] focusing attention on the formation of compact but not crystalline structures. To provide additional insight into the process of polymer crystallization, in this paper we present a simulation study of single polymer molecules through an extension of the CI algorithm to polymer chains which proved able to reproduce the main features of polymer crystallization.

## The Model

The polymer chain is modeled as a self-avoiding walk of a sequence of hydrophobic residues on a square lattice. Each monomer occupies one lattice site, connected to its neighbors and unable to occupy a site filled by any other residue (excluded volume condition). At each point, the chain can turn 90° left or right or can continue ahead. The energy of the molecule is determined by the summation of the favorable energy contribution of −1 units deriving from each contact between two nonbonded residues occupying neighboring nondiagonal lattice points. In the present version of the CI algorithm the energy contribution of −1 is only applied if, in addition to spatial proximity, the two interacting residues both present a linear and parallel arrangement, forming what we can call a linear−linear (LL) interaction (Figure 1A); while contacts which involve corners do not contribute to the energy of the molecule; they are considered as melted parts. Throughout this paper we define as the "LL-loop" the sequence of residues that connects two residues presenting an LL contact interaction. This definition differs from the usual meaning of the word "loop"; in our model a residue can belong also to a number of LL-loops greater than one. The algorithm here presented is called the CI/LL algorithm as it derives from our previous algorithm[7] with a re-definition of the energy associated with the hydrophobic interactions.

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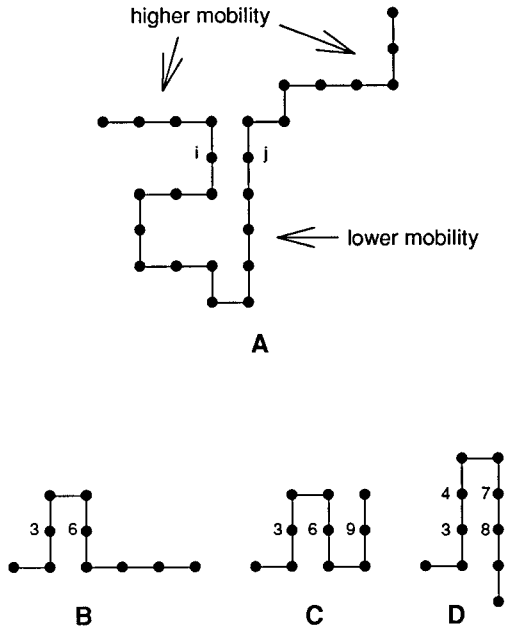


**Figure 1.** A: LL-interaction between residues *i* and *j* of a homopolymer modeled on the 2D square lattice: effects on the mobility of the residues in different portions of the chain. B−D: three conformations of a homopolymer chain model ($N = 10$); conformation B has one LL contact defined by residues 3/6; conformation C has two LL contacts defined by residues 3/6 and 6/9; conformation D has two LL contacts defined by residues 3/8 and 4/7.

The CI algorithm derives from the concept of cooperativity illustrated by Dill et al.[9] to explain the sequential assembly of hydrophobic contacts that leads to compact protein conformations with one or more hydrophobic cores. It relies on the consideration that, when a contact between nonbonded residues is established, e.g., between residues *i* and *j* in Figure 1A, this interaction creates a heterogeneity in the conformational freedom of the different residues of the molecule; all the residues in the loop from *i* to *j* have less mobility than the residues outside them. Accordingly, in the CI/LL algorithm a polymer chain composed of N residues is described in the following way in the 2D space. Each conformation is defined by N-2 internal coordinates $\theta$ which represent the angles at each residue (excluding the two ends): for angles of 90°/180°/−90° $\theta(i)$ can assume the three values 1/0/−1, respectively, according to the fact that the chain turns left, goes ahead, or turns right at the *i*th residue. To take into account the concept of mobility defined above, the CI/LL method associates to each nonterminal residue a cooling factor, $f(i)$, that describes its mobility, i.e., the probability for $\theta(i)$ to change. For a residue not involved in LL-loops the movement is completely free and $f(i) = 0$. When a residue is involved in one or more LL-loops, $f(i) = -n_{LL}$, where $n_{LL}$ is the number of LL-loops in which the residue is involved; in this case, to change $\theta(i)$, an energy barrier has to be passed as a movement at the *i*th residue involves the break of the favorable contact interactions between the residues at the ends of the LL-loops to which the *i*th residue belongs.

In a completely unfolded conformation presenting no LL-loop the energy of the conformation is $E = 0$ and all $f(i) = 0$. In a folded conformation in which $N_{LL}$ contacts are present, $E = -N_{LL}$, but this energy does not determine the behavior of the molecule. Actually, the molecule evolves according to the $f(i)$'s associated with each residue.

**Table 1. Density of States $n(E)$ of the Homopolymer Chain Models P12, P16, and P20**

| | $n(E)$ | | |
|---|---|---|---|
| $E$ | **P12** | **P16** | **P20** |
| 0 | 13306 | 668047 | 32857830 |
| −1 | 1470 | 107684 | 6944522 |
| −2 | 235 | 22409 | 1702883 |
| −3 | 24 | 3293 | 307830 |
| −4 | 2 | 569 | 64433 |
| −5 | | 64 | 9744 |
| −6 | | 9 | 2012 |
| −7 | | | 273 |
| −8 | | | 48 |
| −9 | | | 3 |
| $\sum n(E)$ | 15037 | 802075 | 41889578 |

See, for example, the three conformations B, C, and D of a homopolymer with N = 10 in Figure 1. In conformation B there is only one LL-loop defined by residues 3 and 6, so the mobility of residues 3 to 6 is lowered by one unit while all other residues are free to move. In conformation C there are two LL-loops defined by residues 3,6 and 6,9; it follows that residue 6 has a mobility lowered by two units and residues 3 to 5 and 7 to 9 by one. In conformation D there are two LL-loops defined by residues 3,8 and 4,7; it follows that the mobility of residues 4 to 7 is lowered by two units and of residues 3 and 8 by one.

The following algorithm describes the steps of the CI/LL method.

(1) Start from either an extended or from a randomly generated conformation.

(2) Make a random choice of a residue to be moved, for example the *i*th.

(3) Use a criterion of mobility to decide if it has to be moved or not: move it if $\mathrm{Rnd} < \exp[f(i)/c_k]$, where Rnd is a random number between 0 and 1 and $c_k$ is the "temperature"; if not, count a time step and go to 2.

(4) Make a random choice of the movement, i.e., make a random choice of the value of $\theta(i)$ while taking invariant all the other $\theta$ coordinates (this corresponds to a pivot move).

(5) Check the validity (excluded volume condition) of the structure deriving from the movement; if not valid, count a time step and go to 2.

(6) If the structure is valid, accept the new conformation and evaluate its energy; a time step is counted and the cooling factors $f(i)$ assume the values deriving from the LL-loops present in the new conformation; go to 2.

It should be noted that, though individual steps may imply major rearrangements of the chain due to the move set which is based on pivot moves, this algorithm provides a correct overall kinetic view of the approach toward the state of lowest energy of the molecule.

## Thermodynamic Evaluation

The model described above, though representing a Monte Carlo approach, differs from it mainly because the evolution of the system is not governed by the overall energy $E$ of the system but by the cooling factors $f(i)$. It is important to verify whether the system modeled in this way follows the correct thermodynamics. To this aim, we chose some relatively short polymer models of length $N \leq 20$ residues and performed for them the complete enumeration of the valid structures in two dimensions calculating the corresponding energies. In Table 1 are reported the density of states, $n(E)$, for three chains of length $N = 12$, $N = 16$, and $N = 20$ (**P12**, **P16**, **P20**). It is possible to calculate from $n(E)$

**Table 2. Comparison of the Relative Population of States P($E$, $c_k$) of the Homopolymer Chain Model P20 at the Three Temperatures $c_k$ = 0.3, 0.5, and 1.0[a]**

| | $c_k = 0.3$ | | $c_k = 0.5$ | | $c_k = 1.0$ | |
|---|---|---|---|---|---|---|
| $E$ | a | b | a | b | a | b |
| 0 | 0.0 | 0.0 | 1.7 | 1.6 | 42.8 | 42.7 |
| −1 | 0.0 | 0.0 | 2.6 | 2.6 | 24.6 | 24.6 |
| −2 | 0.0 | 0.0 | 4.7 | 4.5 | 16.4 | 16.4 |
| −3 | 0.0 | 0.0 | 6.2 | 6.2 | 8.1 | 8.4 |
| −4 | 0.1 | 0.1 | 9.7 | 9.8 | 4.6 | 4.4 |
| −5 | 0.3 | 0.2 | 10.8 | 10.5 | 1.9 | 1.9 |
| −6 | 1.8 | 1.8 | 16.5 | 16.5 | 1.1 | 1.0 |
| −7 | 6.7 | 6.0 | 16.5 | 16.4 | 0.4 | 0.4 |
| −8 | 33.1 | 33.7 | 21.5 | 21.8 | 0.2 | 0.2 |
| −9 | 58.0 | 58.2 | 9.9 | 9.9 | 0.0 | 0.0 |

[a] Method a: calculated from the density of states. Method b: determined through simulations $1 \times 10^7$ time steps long with the CI/LL algorithm as averages in the second half of the simulations for 1000 independent molecules.

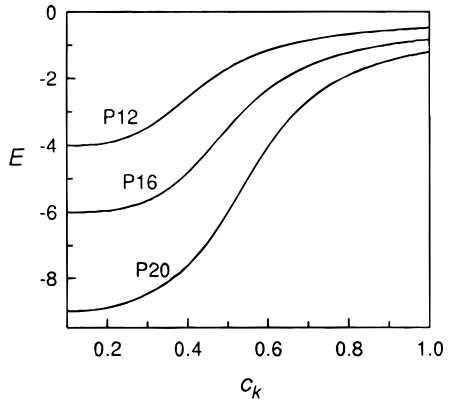


**Figure 2.** Averaged energy ($E$) calculated from a complete enumeration of the valid structures as function of temperature ($c_k$) for the three homopolymer chain models **P12**, **P16**, and **P20**.

the population of states P($E$,$c_k$) at a temperature $c_k$. To do that, the partition function $Z$, which is the sum of the Boltzmann factors over all the conformational states, is required:

$$Z(c_k) = \sum_E n(E) \exp(-E/c_k)$$

The population of states, i.e., the probability that the chain assumes a conformation of energy $E$ at temperature $c_k$ is

$$P(E,c_k) = [n(E) \exp(-E/c_k)]/Z$$

In Table 2 (column a) is reported the population of states for the **P20** chain at the three temperatures $c_k$ = 0.3, 0.5, and 1.0, chosen in order to have a high temperature (at $c_k$ = 1 the state $E$ = 0 is the most populated), a medium temperature, and a low temperature (at $c_k$ = 0.3 the lower state is the most populated) while in Figure 2 are plotted the averaged values of $E$ vs the temperature $c_k$ for the three chains. A transition between an organized state (at low $c_k$) and an unfolded state (at high $c_k$) is observed which allows us to determine the temperature of the transition $T_f$ which resulted in $T_f$ = 0.46, 0.53, and 0.57 for **P12**, **P16**, and **P20**, respectively, while the transition becomes sharper with increasing chain length.

We then performed several simulations with the CI/LL algorithm in the 2D space on **P12**, **P16**, and **P20** which were long enough ($1 \times 10^7$ time steps) to ensure that equilibrium is reached in the first half of the simulation, whereas in the second half data were collected; in Table 2 (column b) are also reported the populations of states obtained as averages from 1000 independent molecules for **P20**. The agreement between these values and those obtained by complete enumeration (column a) is very good, thus indicating that our algorithm obeys the correct thermodynamics derived from the definition of energy. The values obtained for the **P12** and **P16** chains show a similar agreement. Assuming that this holds also for longer chains, it is possible to determine through our algorithm the population of states also for chains of length longer than 20 residues, and chains of even hundreds or thousands of residues can be studied.

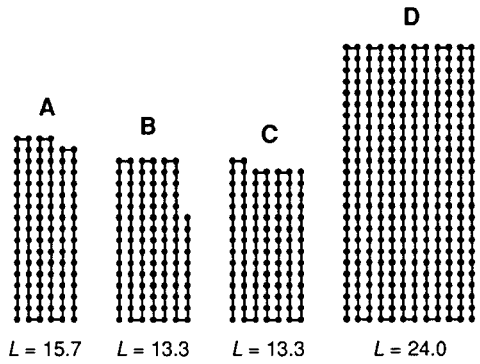


**Figure 3.** Some examples of the minimum energy conformations ($E$ = −73) of the homopolymer chain **P100** (A, B, and C) and the unique minimum energy conformation ($E$ = −253) of the homopolymer chain **P300** (D).

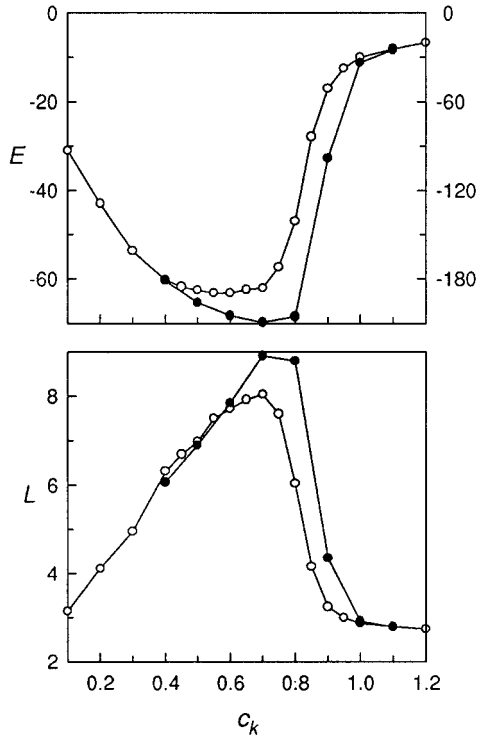


**Figure 4.** Results from simulations $2 \times 10^7$ time steps long with the CI/LL algorithm on the homopolymer chain model **P100** (empty circles) averaged over 100 independent molecules in the last 10% of the simulations: energy ($E$) and thickness ($L$) as function of temperature ($c_k$). The results obtained for **P300** with $6 \times 10^7$ time steps averaged over 30 independent molecules are given as full circles. The left scale in the $E$ plot refers to **P100** and the right one to **P300**.

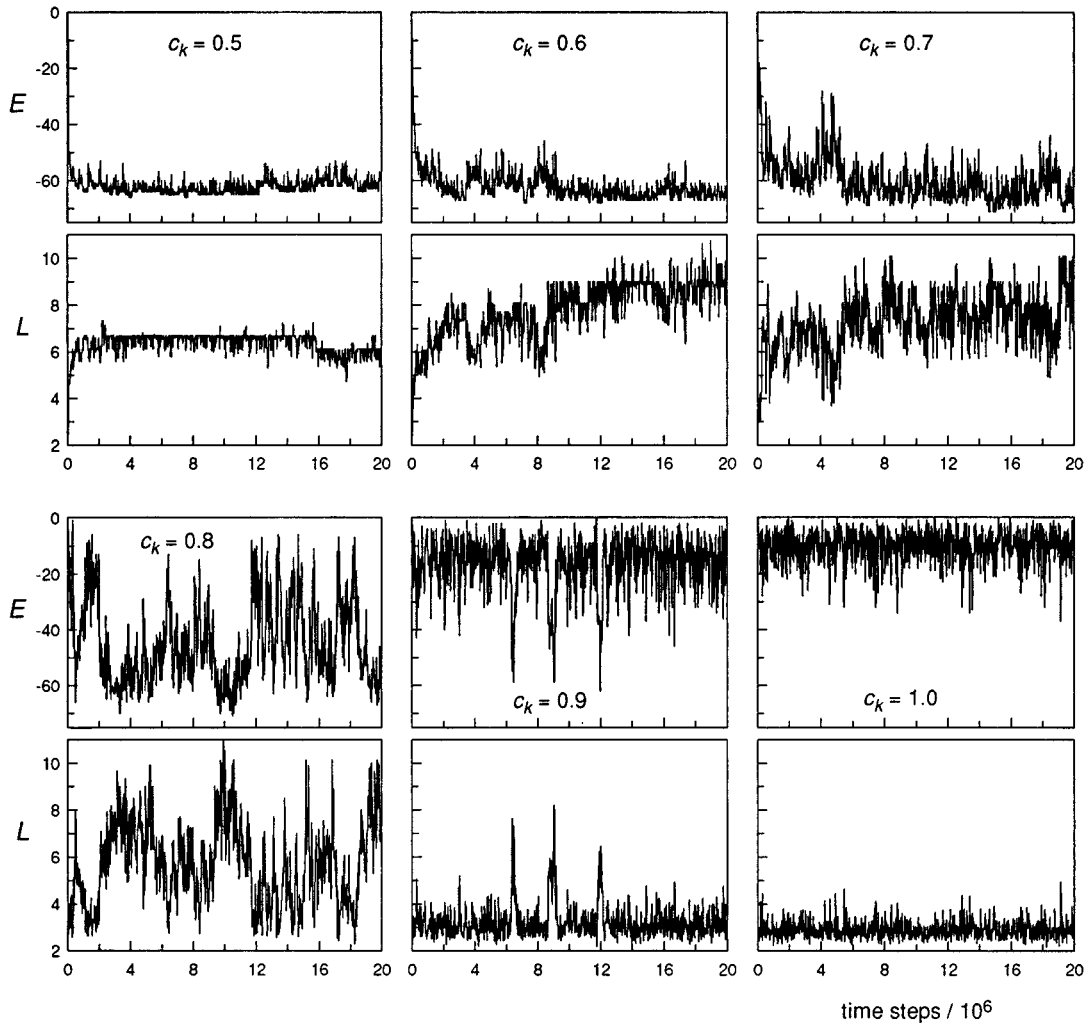


**Figure 5.** Results from simulations $2 \times 10^7$ time steps long with the CI/LL algorithm on the homopolymer chain model **P100** at various temperatures: energy ($E$) and thickness ($L$) as function of time steps for single molecules.

## Results

The simulation approach we have presented has been applied to chains with $N = 100$ and $N = 300$, **P100** and **P300**, respectively. The global minimum of **P100** has energy $E = -73$ and is a highly degenerate ground state; in Figure 3 are reported some of the several possible conformations with this energy. For **P300** the unique minimum energy conformation, also reported in Figure 3, has $E = -253$. To describe these (and other) conformations it is necessary to define some quantities, related to the conformations, which give the numerical value of the "thickness" of the structures. In our opinion, rather than using the averaged length of the linear segments (rods) present in the conformation,[6] it is more useful to utilize the averaged length of rods excluding those of length 1. This parameter, $L$, gives, as can be seen below, a number directly correlatable to thickness of the conformation and can be defined by the equation

$$L = (N - 1 - f_1)/(N_c + 1 - f_1)$$

where $N$ = number of monomers, $f_1$ = number of rods of length 1, and $N_c$ = number of bends, i.e., number of residues at which $\theta(i) = 1$ or $-1$.

In the case of the conformations of **P100** reported in Figure 3, $L = 15.7$, 13.3, and 13.3 for the conformations A, B, and C, respectively.

To determine the influence of molecular weight, we focused first our attention on the chain with $N = 100$, **P100**, for which we tried to obtain a plot of energy as function of $c_k$ similar to those reported in Figure 2. We ran several simulations with the CI/LL algorithm on ensembles of 100 independent molecules choosing always the same duration independently from the temperature ($2 \times 10^7$ time steps). Each simulation started from completely extended conformations which were equilibrated for $2 \times 10^4$ time steps at $c_k = 100$ to give an ensemble of random conformations; then, the temperature was quenched to the value chosen for each simulation. In Figure 4 we report the plot of energy $E$, averaged in the last 10% of the simulations, as a function of $c_k$. At high temperatures the observed behavior is quite similar to that of Figure 2; a transition is observed at a temperature ($T_f = 0.81$) higher than for **P12**, **P16**, and **P20** due to the greater length of the chain in **P100**. At lower temperatures, however, the energy reaches a value of $-62/-63$ in the range of temperatures 0.70−0.45 and then increases again with a further lowering of the temperature. Depending on temperature, we are under a different kind of control. At temperature $c_k \geq 0.75$ the simulations are long enough to reach equilibrium so that the results reflect a thermodynamic control. At $c_k < 0.75$ the simulations are too short to reach equilibrium; the system has slow kinetics and presents a glassy behavior. We have

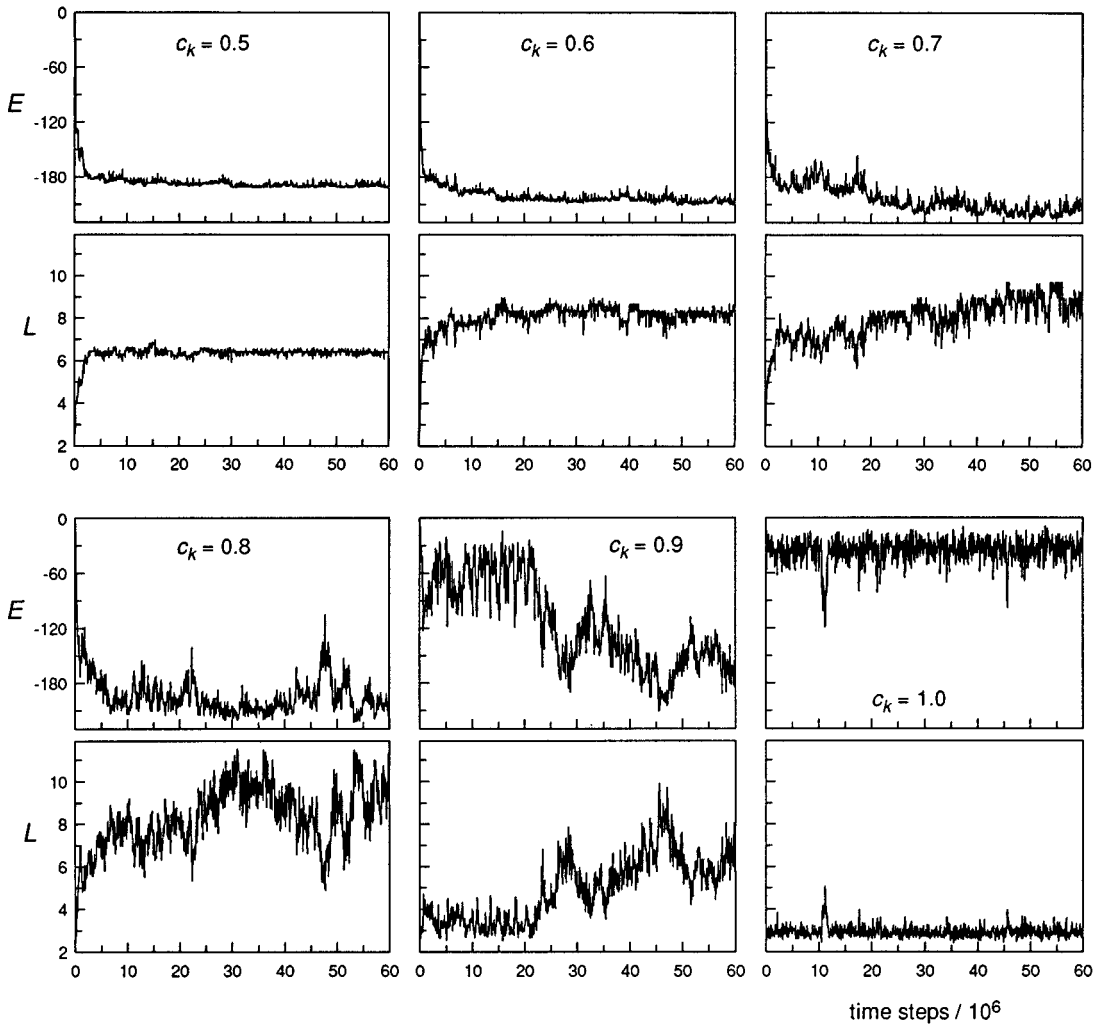


**Figure 6.** Results from simulations $6 \times 10^7$ time steps long with the CI/LL algorithm on the homopolymer chain model **P300** at various temperatures: energy ($E$) and thickness ($L$) as function of time steps for single molecules.

determined the mean values of $L$ averaging the values of the 100 independent molecules in the last 10% of the time. A dependence from the temperature quite similar to that of $E$ was observed (Figure 4). At high temperatures $E$ is high and $L$ is very low (at $c_k = 1.2$, $E = -6.6$ and $L = 2.74$; at $c_k = 1.0$, $E = -10.0$ and $L = 2.87$). These values are slightly different, in particular the energy, from the values determined for a completely random ensemble of molecules with no attractive force between residues ($E = -1.8$ and $L = 2.61$) indicating that at these values of temperature, rather than a completely random coil, slightly collapsed structures are present.

The sharp transition at $c_k = 0.81$ is also observed in the $L$ plot and separates the region of high temperatures from the region in which compact structures do exist. $L$ assumes its maximum value at $c_k = 0.70$ and then becomes smaller and smaller with decreasing temperature. It is worthy to point out that while the lowest energy conformations of **P100** have $L = 13-16$ (Figure 3), the maximum averaged value that is reached at $c_k = 0.70$ is $L = 8.05$. This value does not represent the equilibrium value at $c_k = 0.70$ but is very close to it, as demonstrated by the fact that by performing a longer simulation ($5 \times 10^7$ time steps), $L$ becomes slightly higher ($L = 8.47$), but a further increase of the time ($1 \times 10^8$ time steps) does not influence it ($L = 8.49$). This fact indicates that at temperatures below $T_f$ (e.g. $c_k = 0.70$) the minimum of free energy occurs for values of energy higher than $-73$ and for values of $L$ smaller than $13-16$ as the entropy of the system favors conformations with a shorter thickness. The "annealing" at constant temperature is also observed for temperatures lower than 0.70 (e.g., at $c_k = 0.60$: $L = 7.72$ with $2 \times 10^7$ time steps; $L = 8.01$ with $5 \times 10^7$ time steps; $L = 8.30$ with $1 \times 10^8$ time steps) but the effect becomes less pronounced with decreasing temperature (e.g. at $c_k = 0.50$: $L = 6.97$ with $2 \times 10^7$ time steps; $L = 7.21$ with $5 \times 10^7$ time steps; $L = 7.31$ with $1 \times 10^8$ time steps) and at $c_k = 0.30$ is no longer observed. Moreover, at a temperature lower than 0.70, $1 \times 10^8$ time steps are no longer sufficient to reach equilibrium as kinetics are too slow. So, the progressive lowering of $L$ while lowering $c_k$ depends on the increased slowing of kinetics at low $c_k$.

Further information can be obtained by analyzing the evolution of single molecules at various temperatures by following how $E$ and $L$ vary with time. Figure 5 reports the corresponding plots obtained for single molecules of **P100** chosen from the ensembles of 100 molecules of the previously described simulations for several temperatures. At high temperatures (e.g. $c_k = 1.0$) from the randomly generated conformations a slightly collapsed structure is obtained which dynamically fluctuates around values of about $E = -10$ and $L = 2.9$. At low temperatures (e.g. $c_k = 0.70$), without

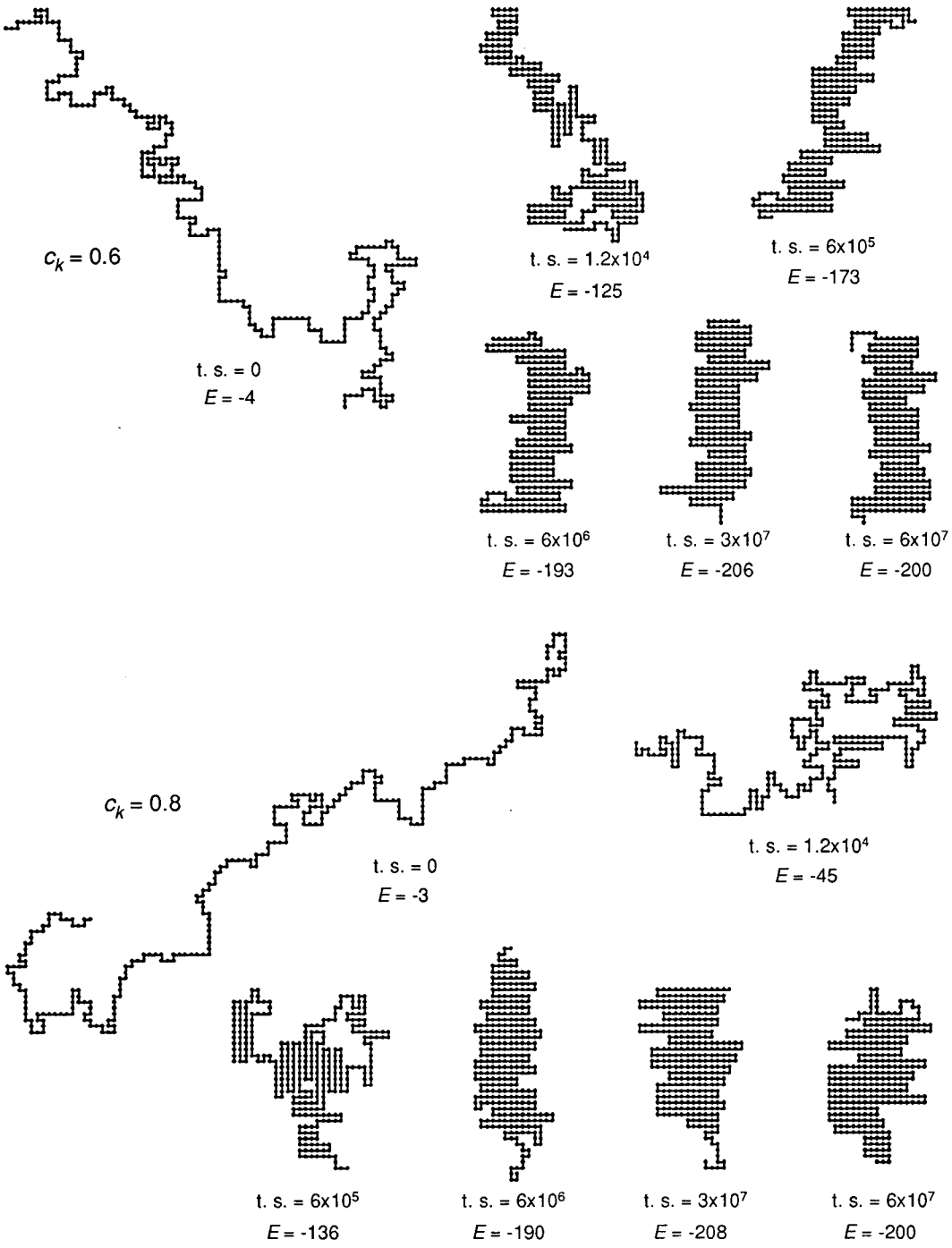


**Figure 7.** Results from simulations $6 \times 10^7$ time steps long with the CI/LL algorithm on the homopolymer chain model **P300**. Conformational "story" of two single molecules at $c_k = 0.60$ and at $c_k = 0.80$. The minimum energy conformation ($E = -253$) shown in Figure 3 is never attained.

passing from the slightly collapsed structure, a compact state is obtained which dynamically fluctuates around the values of $L = 8$ and $E = -60$. At intermediate temperatures (e.g. $c_k = 0.80$) a two state equilibrium between the slightly collapsed structure ($E = -20$, $L = 3-4$) and the compact state ($E = -60$, $L = 8$) is observed. At very low temperatures (e.g. $c_k = 0.50$) almost all degrees of freedom have been lost, and the molecule presents only small fluctuations, most likely at the ends of the chain.

The present study was then extended to the chain composed of 300 residues (**P300**) for which a series of simulations at various temperatures under the same conditions already used for **P100** except that a duration three times longer ($6 \times 10^7$ time steps) was carried out. Figure 4 reports the corresponding plots of energy ($E$) and thickness ($L$) as function of temperature ($c_k$) which appear quite similar to those shown in the same figure for **P100**. The transition occurs at $c_k = 0.85$; the plot of energy has the same shape in both cases and the minimum value of $E$ is $-210$, i.e., about three times as for **P100**. The plot of $L$ shows a maximum with about the same height determined for **P100**, $L = 8-9$, i.e., the chain length does not significantly influence the thickness but only the energy. It is worth pointing out that the unique minimum energy conformation of **P300** has $E = -253$ (Figure 3), and the thickness $L = 8-9$ is considerably shorter than that corresponding to the

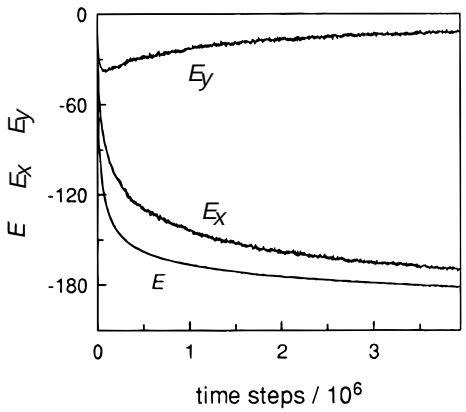


**Figure 8.** Results from simulations $4 \times 10^6$ time steps long with the CI/LL algorithm on the homopolymer chain model **P300** at $c_k = 0.50$ averaged over 1000 independent molecules. Energy ($E$) and the distinct contributions to energy of the loops in the preferred direction ($E_x$) and the other direction ($E_y$) as function of time steps.

global minimum of energy ($L = 24$). Figure 6 reports the plots of $E$ and $L$ vs time steps obtained for single molecules of **P300** analogous to those of **P100** in Figure 5, while in Figure 7 are reported, for the temperatures $c_k = 0.60$ and $c_k = 0.80$, some selected conformations from the plots of Figure 6 which put into evidence the conformational "story" of single molecules. Starting from the random conformations obtained at the end of the preequilibration period (time steps = 0), a first collapse is initially obtained with formation of loops and nuclei of "crystallization" casually oriented in the horizontal and vertical direction. Some of the nuclei then grow at the expense of the others and after about $6 \times 10^5$ time steps at $c_k = 0.60$ and $6 \times 10^6$ time steps at $c_k = 0.80$ lamellar structures are formed. So, the process of attainment of crystals from random coils originates in two steps: a fast collapse to give a compact globule, such as the one obtained at $6 \times 10^5$ time steps at $c_k = 0.80$ (Figure 7), followed by a slow rearrangement to give lamellar structures.

As an attempt to give a more detailed picture of this two-stage process, in Figure 8 is reported the plot of $E$ averaged over 1000 molecules in a simulation at $c_k = 0.50$ that is $4 \times 10^6$ time steps long. A sharp initial decrease in $E$ to $-150$ in the initial $3 \times 10^5$ time steps is followed by a slower further decrease from $-150$ to $-180$ attained after $4 \times 10^6$ time steps. The two processes can be kinetically distinguished by a curve fit with a two-exponential equation ($E = a_0 + a_1 e^{-\lambda 1 t} + a_2 e^{-\lambda 2 t}$) which gives $\lambda_1 = 3.64 \times 10^{-5}$ and $\lambda_2 = 1.29 \times 10^{-6}$. In Figure 8 are also reported the distinct contributions to energy of the loops in the preferred direction, $E_x$, and the other direction, $E_y$. It can be seen that $E_x$ and $E_y$ drop initially simultaneously, indicating a first collapse to an unorganized globule. Then, $E_x$ increases at the expenses of $E_y$, becoming largely preferred in the crystalline state. Also $E_x$ can be fitted with a two-exponential equation, giving $\lambda_1 = 2.28 \times 10^{-5}$ and $\lambda_2 = 0.98 \times 10^{-6}$, both lower than the corresponding constants determined for $E$. Energy $E$ can be considered a parameter for compactness and $E_x$ for lamellarity. Thus, the kinetics for the attainment of compact states are faster than the kinetics for achieving lamellar structures.

## Discussion

The CI/LL method is proposed as an algorithm for the simulation of homopolymer chains modeled on a square lattice. The model proved very efficient in reproducing the main features of homopolymers under crystallization conditions, including the formation of lamellar structures by individual molecules. The lamellar thickness has been shown to be rather independent of chain length but strongly dependent on the temperature of the simulation. A two-phase process was evident: first a collapse to a random collapsed globule followed by a rearrangment to the final lamellar molecule. It is striking that individual molecules acquire this structure without the need of an external crystallization nucleus.

The method evidenced the importance of entropic factors which make structures with a thickness of 8−9 units thermodynamically preferred, at temperatures just below the transition point, over structures with higher thickness which represent the global minimum of energy but not the global minimum of free energy. The observed decrease (both in experiments and in our model) of the lamellar thickness with decreasing temperature is due to a kinetic reason because at low temperatures molecules are entrapped in structures of low thickness which can only slowly increase with time (annealing).

In the simulation presented in this paper individual molecules have been studied on a 2D square lattice. Work is in progress to extend the model to the 3D cubic lattice; preliminary results indicate that the behavior is quite similar to the behavior described in two dimensions. It is logical to question what will happen when a random coil or a partially collapsed globule is allowed to collapse on the surface of a crystal. Preliminary simulations show that the presence of the crystal does not have much influence on the behavior we have described. Further simulations are required in order to determine the details of this process. Large molecules might grow simultaneously on different regions of an individual crystal.

The simulations presented may be directly aplicable to polymers in solution. In the melt the same principles should apply, but the presence of entanglements will play a major role. Regions between entaglements may collapse into globules which will then become partially crystalline, with entaglements located in poorly ordered interlamellar regions.

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