

A Molecular Dynamics Study of Linear Bead–Spring Polymer Chain Self-Organization into Condensed Amorphous and Crystalline Globules

Tatiana V. Vorobyeva,^a Alexander I. Melker,^a Kenneth D. Knudsen^{†,b}
and Arnljot Elgsaeter^b

^aPhysics and Mechanics Faculty, St. Petersburg State Technical University, St. Petersburg, 195251 Russia and ^bDepartment of Physics, University of Trondheim, Norwegian Biopolymer Laboratory (NOBIPOL), NTH, N-7034 Trondheim, Norway

Vorobyeva, T. V., Melker, A. I., Knudsen, K. D. and Elgsaeter, A., 1996. A Molecular Dynamics Study of Linear Bead–Spring Polymer Chain Self-Organization into Condensed Amorphous and Crystalline Globules. – Acta Chem. Scand. 50: 18–23 © Acta Chemica Scandinavica 1996.

The self-organization of extended linear polymer chains into condensed globules has been studied using molecular dynamics methods. In this study we have used a bead–spring polymer model with 100 beads in which each bead has three degrees of freedom. The interaction between all beads is modelled using the Morse potential, but this interaction is assumed to be 25 times stronger for topological nearest neighbours along the polymer chain than for topological non-nearest neighbours. We find that the condensed chains (globules) are amorphous or crystalline depending on the relative length of the equilibrium distances for the non-nearest-neighbour interactions.

The structures of crystalline and amorphous polymers are usually analyzed separately because the two different forms are regarded as separate condensed states with their own mechanisms of molecular packing.^{1,2} However, the condensed polymer may also be considered as a mixture of crystalline and anticrystalline clusters.³ The latter approach does not specify the morphology inside the clusters, but does treat amorphous and crystalline states of the condensed polymer on a common ground. The well developed traditional methods of theoretical physics are, however, of limited help in this case because it is not known how to formulate detailed quantitative mathematical descriptions of the various qualitative models suggested.² Currently the most promising approach to analyzing this problem is therefore the use of computer simulation. Using molecular dynamics methods it is in principle also possible to carry out detailed simulations for atomic polymer models, but it is expected that the main characteristics of polymer chain condensation can be obtained using simpler and more coarse-grained models.^{4–6} The latter models have the advantage that in addition to requiring less computer time they are also more tractable analytically.

In this paper we report on a study of the three-dimensional self-organization of extended linear bead–spring polymer chains into condensed globules using molecular dynamics methods. Each bead in the bead–spring chain has three degrees of freedom. The main distinction between the polymer model used in this study and that used earlier⁵ is related to the choice of potentials for the interactions between beads that are not topological nearest neighbours in the polymer chain.

In the case of biopolymers, when performing simulation studies of their dynamic properties, the method of simulation and the complexity of the model is related to the characteristic times of change for the properties under study. For instance, to simulate the fast fluctuations in the equilibrium atomic structure of a globular protein, a detailed atomic model of the protein is used, with empirically parametrized terms corresponding to contributions from bonds, bond angles, hydrogen bonds, etc.⁷ In this case the molecular dynamics method of simulation is appropriate. To simulate slower processes, as for instance large-scale conformation changes such as protein denaturation or folding, one can use a model where many structural details are neglected.⁸ This is because, on the timescale of interest, the fast local motions mentioned above are assumed to be averaged to zero. The residues can then be presented by, for instance, spheres which are linked by virtual bonds, and one can use simplified expressions for the interaction potentials.⁹ The reduced

[†] To whom correspondence should be addressed. Present address: Departamento de Química Física, Universidad de Murcia, 30071 Murcia, Spain.

number of degrees of freedom allow rapid calculation of forces so that simulations sufficiently long to cover the timescale of interest are feasible. Simulations of this type can be performed with the molecular dynamics method, but also Monte Carlo methods can be used.^{10,11} Although in the present work the purpose has not been to study one biopolymer in particular, the simulation has been of the abovementioned type, using a simplified polymer model and the molecular dynamics simulation method. Our study has been performed in vacuum, i.e. the only interactions present are interactions between the beads in the model. However, if we had wanted to include the effect of a solvent, it would be possible to use the technique of Brownian dynamics simulation,^{12,13} where the solvent viscosity is introduced and the random movements of the solvent molecules are replaced by a stochastic force.

The purpose of the present work has been to study the basic properties of linear chains when they collapse, and to see if variation in equilibrium distances for non-nearest neighbour interactions in the polymer chain can help to explain its different three-dimensional structures. We find

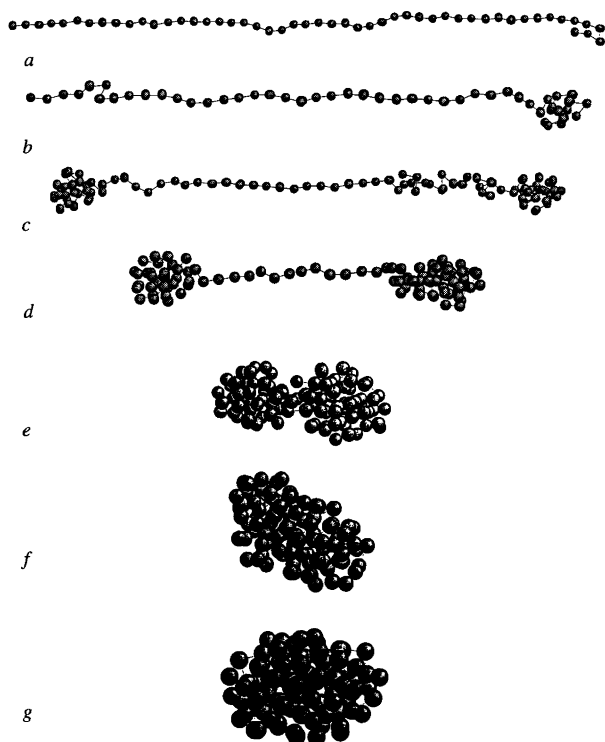


Fig. 1. Time evolution of the spontaneous folding of an anharmonic linear bead-spring chain into a compact globule. The equilibrium distance for the interaction between nearest neighbours, r_0 , next-nearest neighbours, r_1 , second-nearest neighbours, r_2 , etc. are all equal ($r_0=r_1=r_2=\dots$). A representative selection of conformations as function of time is shown in (a)–(g). The number of integration steps between each of the conformations shown was from 1000 to 6000 (see Fig. 2). Note that in (a) and (b) only the right half of the chain is shown. The final stage corresponds to 15000 integration steps.

that these variations play an important role in determining whether polymer self-organization leads to formation of amorphous or crystalline globules, respectively.

Polymer model and simulation procedure

In our numerical simulation studies we used a bead-spring polymer model with 100 beads, where each bead has three degrees of freedom. The interaction between all beads is modelled using the anharmonic Morse potential

$$V(r) = V_0 \{ \exp[-2\alpha r_0(r/r_0 - 1)] - 2\exp[-\alpha r_0(r/r_0 - 1)] \} \quad (1)$$

where $\alpha r_0 = 39.0$, r_0 being the equilibrium distance between beads and α an interaction parameter. The parameter V_0 equals 0.34 eV for a nearest-neighbour interaction. The interaction is, however, assumed to be 25 times as weak for topological non-nearest neighbours along the polymer chain as for topological nearest neighbours, and the potential in eqn. (1) is therefore reduced by a factor of 25 for non-nearest neighbours. The strong potential serves the purpose of defining the nearest-neighbour distance. We have studied three different combinations of equilibrium distances for the interaction between pairs of beads.

Case 1: The equilibrium distance is the same for the interaction between any pair of beads, i.e. $r_0 = r_1 = r_2 = \dots$, where r_0, r_1, r_2, \dots equal the equilibrium distance for topological nearest neighbours, next-nearest neighbours, second-nearest neighbours, and so on.

Case 2: Equilibrium distance $r_1 = r_2 = r_3 = \dots = \sqrt{2} r_0 = 1.414 r_0$.

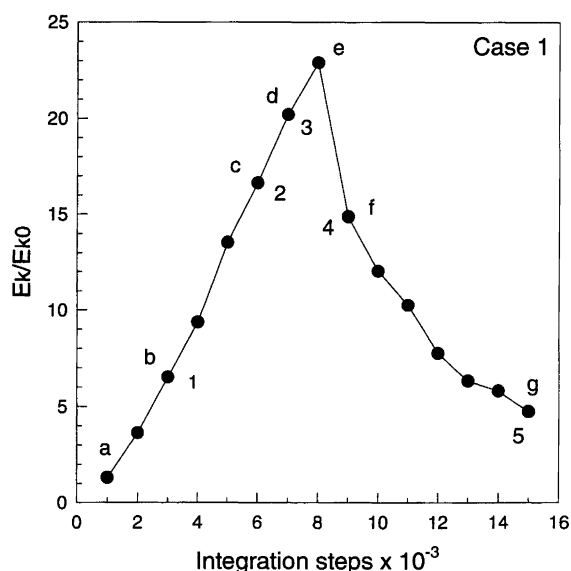


Fig. 2. The relative kinetic energy of the bead-spring chain described in Fig. 1 as a function of the number of integration steps. E_{k0} is the kinetic energy of the starting configuration. Labels (a)–(g) refer to the various conformations shown in Fig. 1.

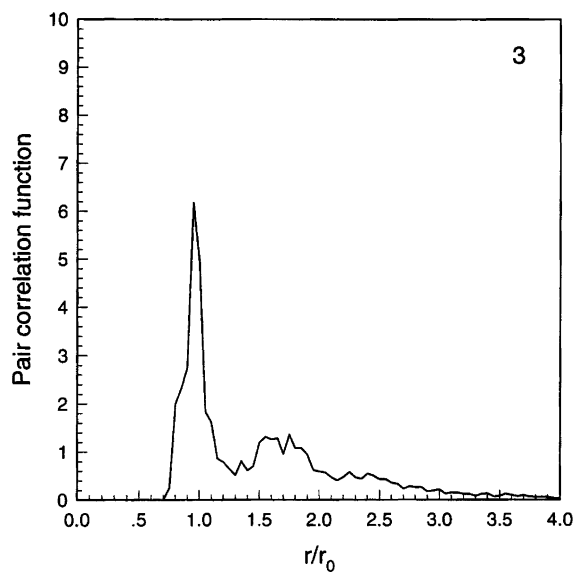
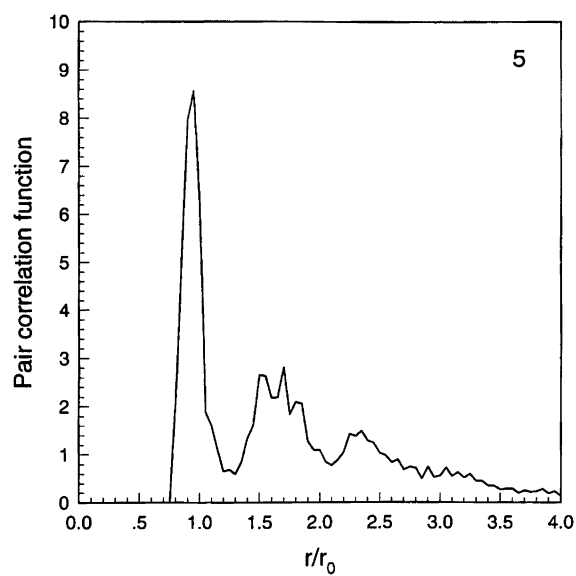
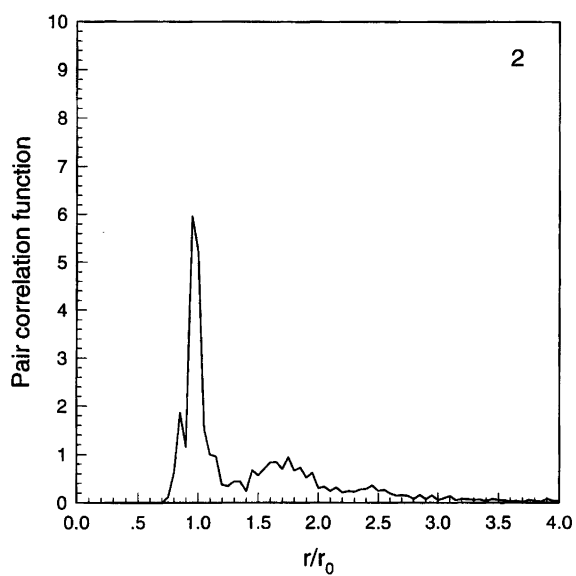
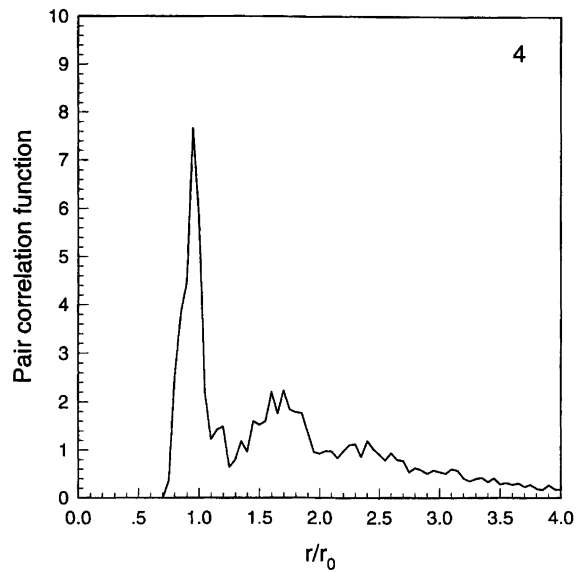
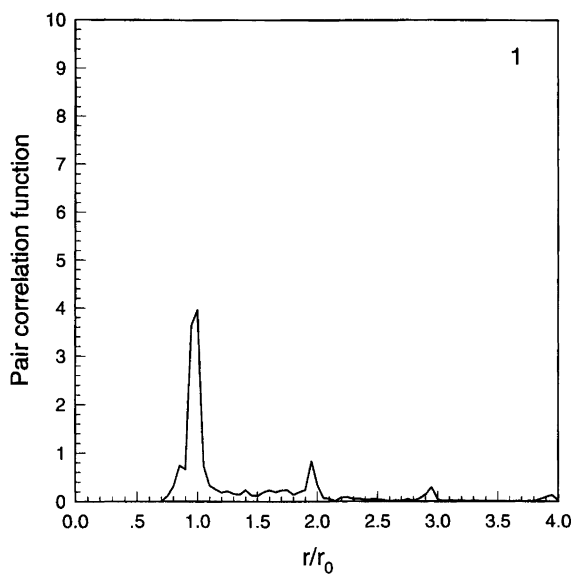


Fig. 3. The pair correlation function vs. r/r_0 for different stages of the spontaneous folding of the bead-spring chain shown in Fig. 1. Correlation functions 1–5 correspond to the times marked 1–5 in Fig. 2.

Case 3: Equilibrium distance $r_1 = \sqrt{2} r_0$ and $r_2 = r_3 = \dots = r_0$.

The bead-spring chain is first brought to thermodynamic equilibrium with a kinetic energy corresponding to a temperature of $158 \text{ K mol kg}^{-1}$ by picking the velocities of each bead from a Maxwell distribution at that temperature. Under these conditions it takes 2–5 periods of bead vibrations to reach a state of thermodynamic equilibrium, which criterion is the fulfilment of the condition.¹⁴ $\langle \Delta T^2 / T^2 \rangle \leq 1/3N$, where T is the temperature and N the number of beads. After this, the nucleation and evolution of the structure that appears as the chain condenses is studied using molecular dynamics methods. The Newtonian equations of motion are integrated numerically using the Nordsieck method¹⁵ to the fifth order of accuracy. The optimum time step is equal to $1/22$ of the bead vibration period in order to fulfill the requirement of conservation of the total energy of the beads.¹⁶ One evolution history comprises approximately 750 periods of bead vibrations, and computing time does not exceed 2 h on a 486, 33 MHz PC with 4 Mbyte RAM. To perform the simulations we used the computer program BELINDA¹⁷ written in C. During the evolution of the chain folding the change in kinetic energy is calculated. In addition, the pair correlation function for the chain is calculated by means of eqn. (2)

$$g(r) = \frac{1}{N/V} \frac{n(r)}{4\pi r^2 \Delta r} \quad (2)$$

where N/V is the average density of beads and $n(r)$ is the total number of beads situated at a distance between r and $r + \Delta r$ from a given bead.¹⁸

All the calculations were made on an IBM PC 486. In other respects the numerical procedure used in this study is similar to that used previously.^{5,6}

Results

The time evolution of the spontaneous folding of an anharmonic Case 1 linear bead-spring chain into a compact globule is shown in Fig. 1. The folding starts at the free ends of the polymer chain (Figs. 1a and 1b), proceeding to form larger and larger bead sub-globules (Figs. 1c–1e) until the two sub-globules merge into one large condensed globule (Figs. 1f and 1g). The condensation of the individual sub-globules is accompanied by kinetic energy growth, but as the sub-globules merge the kinetic energy of the system falls again (Fig. 2). The pair correlation function at first gives evidence of an initial linear structure which can be recognized by small maxima at $r/r_0 = 2$ and 3 (Fig. 3, correlation function 1), where r is the distance between beads. Subsequently, new peaks appear for $r/r_0 = 1.4$ – 2.0 (Fig. 3, correlation functions 2 and 3). These maxima are manifestations of the new structure appearing as the sub-globules are formed (Figs. 1c and 1d). At long times, the pair correlation function trans-

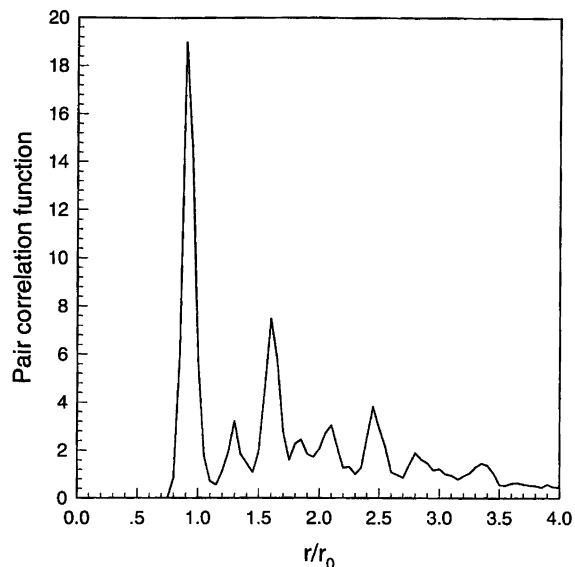


Fig. 4. Correlation function for a perfect face-centered cubic lattice at a kinetic energy corresponding to a temperature of $158 \text{ K mol kg}^{-1}$.

forms into a shape (Fig. 3, correlation functions 4 and 5) which resembles that of a close-packed face-centered cubic crystal lattice (Fig. 4).

The time evolution of the spontaneous folding of an anharmonic Case 2 linear bead-spring chain into a com-

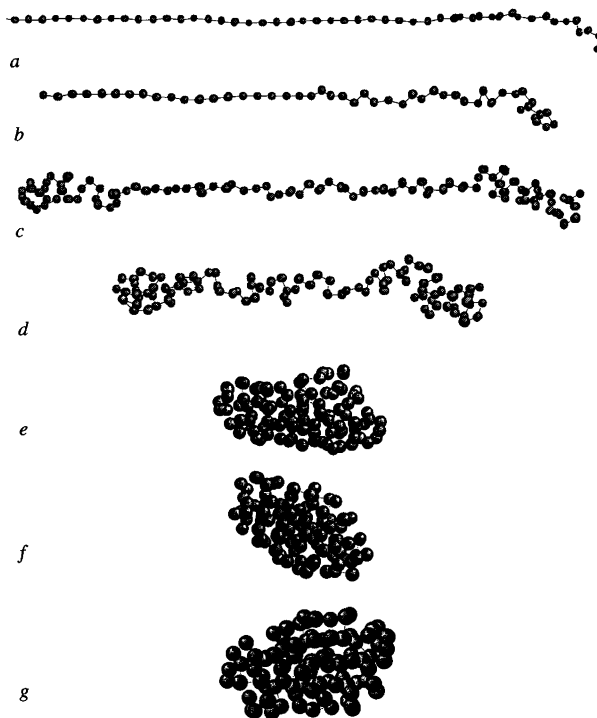


Fig. 5. Time evolution of the spontaneous folding of the same linear bead-spring chain as described in Fig. 1, except that $r_1 = r_2 = r_3 = \dots = \sqrt{2} r_0$.

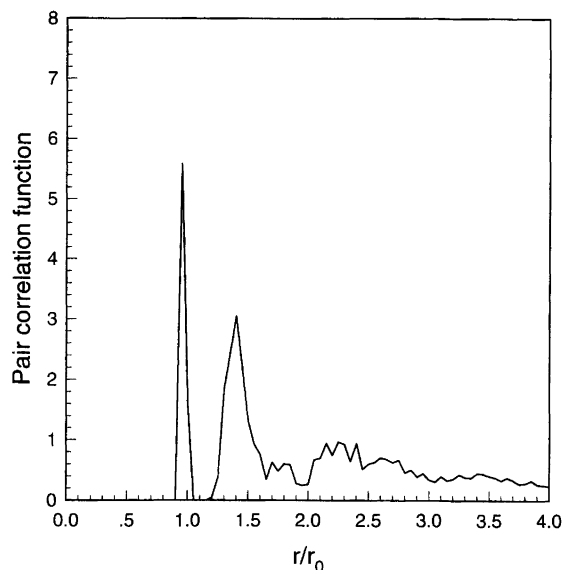


Fig. 6. The pair correlation function vs. r/r_0 after completion of the spontaneous folding of the bead–spring chain shown in Fig. 5.

compact globule is shown in Fig. 5. Also in this case the folding of the chain begins at the free ends (Figs. 5a and 5b), but the formation of distinct sub-globules at the end is much less pronounced than for Case 1 (Fig. 5c), and the folding is more uniformly distributed along the chain (Fig. 5d). It is further noted that the beads in the sub-globules as well as in the final globule are more loosely packed (Figs. 5e–5g) than for the globules shown in Fig. 1 for Case 1. The kinetic energy evolution of the polymer chain (not shown) is qualitatively similar to that shown in Fig. 2 for Case 1, but the time development of the pair correlation function is quite different. From the very beginning a new maximum appears at $r/r_0 = 1.4$, which corresponds to the second coordination sphere. The peak increases monotonically as the polymer condenses. Figure 6 shows the pair correlation function of the fully condensed globule, which equals what is typical for an amorphous material.

With regard to the time evolution of the spontaneous folding of an anharmonic Case 3 linear bead–spring chain into a compact globule (not shown), the evolution was similar to that of Case 2. The time evolution of the temperature was seen to be qualitatively similar to that of the two preceding cases, whereas the pair correlation function of the condensed chain strongly resembled the correlation function for Case 1 (Fig. 3, correlation function 5).

Discussion

The results of our investigation show the following: Firstly, there is no radical difference in the time evolution

of the condensation of an anharmonic chain of beads into a crystalline or into an amorphous globule. Secondly, a change in the equilibrium distance in the weak non-nearest neighbour pair interaction potential has drastic consequences for the final structure of the condensed polymer chain globule and determines whether the final structure is crystalline or amorphous.

It appears that most of the differences in the structures of the condensed polymers can be accounted for by geometrical considerations of polymer packing. The critical aspect seems to be the compatibility of the details of the structure that minimizes the internal energy associated with the strong nearest-neighbour interactions and the structure that minimizes the energy associated with weak non-nearest neighbour interactions. With compatibility we mean how good different structural elements can intermix without giving rise to voids or distortions in the lattice. To try to explain the condensation in the simulated three-dimensional case, for simplicity we will illustrate the abovementioned point by looking at condensation of polymer chains in two dimensions.

In Case 1 is complete compatibility between the structures that maximize all nearest-neighbour and all non-nearest-neighbour interactions. As a consequence the chain can be folded compactly into a crystal with a triangular lattice, obtaining complete packing without distortion (Fig. 7a). Here we have only two possible elements: (1) a straight linear structure and (2) a 60° zigzag structure. Note that these two structural elements are compatible in that they can intermix without giving rise to voids or distortions in the lattice. One may, however, experience kinetically trapped voids. When the two sub-globules that meet are about to merge into one large globule the surfaces of the two sub-globules that come in contact are unlikely to match structurally. This will at least initially give rise to kinetically trapped vacancies in the lattice structure and contribute to non-zero values of the space correlation function for distances not corresponding to ideal face-centered cubic lattice.

In Case 2 there are three structural elements: (1) a trapezoid zigzag structure (Fig. 7b), (2) a straight linear structure (Fig. 7c) and (3) a staircase zigzag structure (Fig. 7e). All these elements are incompatible with one another and can coexist only in the form of short distorted elements. As a consequence, we have a loose amorphous structure with heavily distorted and incompatible structural elements.

In Case 3 there are also three structural elements: (1) a straight linear structure, (2) a 90° zigzag structure and (3) a staircase zigzag structure (Figs. 7c–7e, respectively). Here only a stack of slightly distorted parallel staircase zigzag structures can form a compact cubic crystal. The other elements are not compatible with a staircase zigzag structure, so they will represent folding faults. The difference between Case 3 and Case 1 is the difference in equilibrium distance for the second-nearest neighbours. The difference between Case 3 and Case 2 is the difference in equilibrium distance for the third and all higher-

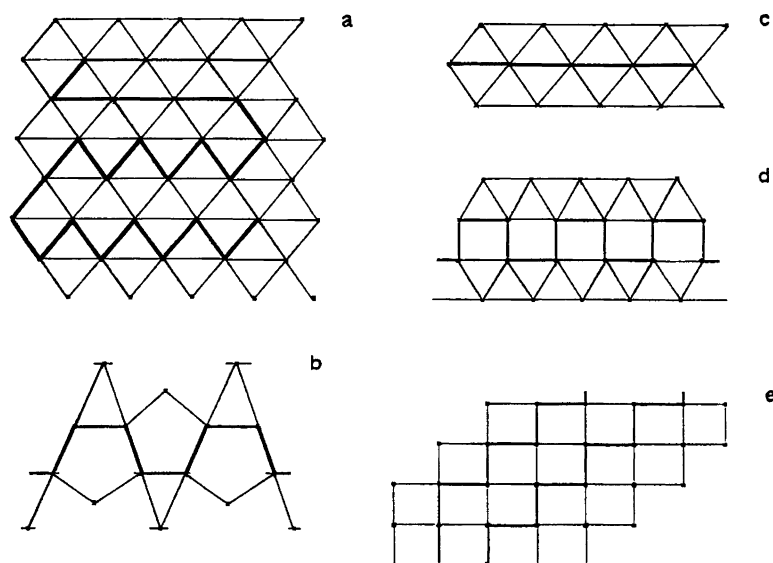


Fig. 7. Compact packing of polymer chains in two dimensions involves several possible basic structural elements: (a) Coexisting straight lines and 60° zigzags on a triangular lattice. Note that these two structural elements are fully compatible in that they can coexist without giving rise to lattice distortions or voids (dense packing). (b) Trapezoidal zigzag on a triangular lattice. These structural elements are incompatible in that they can not give rise to void-free packing. (c) Straight parallel lines on a triangular lattice (dense packing). (d) 90° zigzag on a triangular lattice (dense packing). (e) Staircase zigzags on a square lattice (dense packing).

order neighbours. Case 3 may therefore be viewed as an intermediate between Case 1 and Case 2. It is here of interest to note that the time evolution of the chain structure for Case 3 during condensation is similar to that of Case 2, whereas the development of the pair correlation function strongly resembles that of Case 1.

Conclusion

We have considered the importance of the bead-bead interactions on the self-organization of bead-spring polymer chains. As the polymer chain folds and becomes more condensed different structural elements can be observed. These elements are short straight linear structures and triangular- and right-angled zigzag structures. When these structural elements are completely compatible with one another a perfect crystalline structure can form. However, if they are not compatible a non-perfect crystalline structure appears with irregular structures in between the regions of compatible structural elements. Condensation of a polymer chain that yield only incompatible structural elements results in a final globule with amorphous structure.

Acknowledgement. We thank Morten Meeg and Paal Skjetne, Department of Physics, University of Trondheim, Norway, for assistance with producing graphical pictures of the polymer configurations.

References

1. Allcock, H. A. and Lampe, F. W. *Contemporary Polymer Chemistry*, Prentice-Hall Inc., New Jersey 1981.
2. Privalko, V. P. *Molecular Structure and Properties of Polymers*, Khimia, Leningrad 1986.
3. Perepechko, I. I. *Introduction to Polymer Physics*, Khimia, Moscow 1978.
4. Melker, A. I. *Modeling Experiment*, Znaniye, Moscow 1991.
5. Melker, A. I., Vorobyeva, T. V. and Govorov, S. V. *Sov. Phys. Solid State* 33 (1991) 42.
6. Melker, A. I., Govorov, S. V. and Bungov, V. N. In: Likhachev, V. A., Ed., *Actual Problems of Strength, Proc. 25 All-Union Seminar*, Staraya Rusa, Novgorod 1991.
7. McCammon, J. A. and Karplus, M. *Annu. Rev. Phys. Chem.* 31 (1980) 29.
8. Levitt, M. and Warshel, A. *Nature (London)* 253 (1975) 694.
9. Levitt, M. *J. Mol. Biol.* 104 (1976) 59.
10. Skolnick, J., Kolinski, A. and Yaris, R. *Proc. Natl. Acad. Sci. USA* 85 (1988) 5057.
11. Covell, D. G. *Proteins: Structure, Function and Genetics* 14 (1992) 409.
12. Ermak, D. L. and McCammon, J. A. *J. Chem. Phys.* 69 (1978) 1352.
13. López Cascales, J. J., Navarro, S. and García de la Torre, J. *Macromolecules* 25 (1992) 3574.
14. Landau, L. D. and Lifshitz, E. M. *Statistical Physics (in Russian)*, Nauka, Moscow 1964.
15. Nordsieck, A. *Math. Comput.* 16 (1962) 22.
16. Melker, A. I., Mikhailin, A. I., Likhodedov, N. P. and Ussov, O. A. *FTI Acad. Sci. USSR*, Paper No. 661 (1980).
17. The program 'Belinda' is available at the department of Metal Physics, St. Petersburg State Technical University, USSR.
18. Rahman, A. *Phys. Rev.* 136 (1964) A405.

Received March 5, 1995.