

Short discussion of static properties of dense polymer melts in two dimensions – CMA Monte Carlo Simulation vs Molecular Dynamics

P. Polanowski¹, J.K. Jeszka²

¹ *Department of Molecular Physics
Łódź University of Technology, 90-924 Łódź, Poland
E-mail: piotr.polanowski@p.lodz.pl*

² *Department of Man-Made Fibres
Łódź University of Technology, 90-924 Łódź, Poland
E-mail: jeremiasz.jeszka@p.lodz.pl*

Received: 25 November 2020; revised: 9 December 2020; accepted: 11 December 2020; published online: 17 December 2020

Abstract: In this paper we present the results of an extensive Monte Carlo lattice simulation of two dimensional dense athermal polymer solutions using the Cooperative Motion Algorithm (CMA). Simulations were performed for a wide range of polymer chain length N which varies from 32 to 1024 and for high concentration of polymer. Our results were compared with those obtained by means of molecular dynamics [1].

Key words: Cooperative Motion Algorithm, lattice Monte-Carlo simulations, polymer melts, thin films, structure factor of a polymer chain

I. INTRODUCTION

Behavior of polymer chains in two dimensional systems has been attracting considerable interest in the recent years [2–9]. It is important for understanding of the properties of macromolecules strongly adsorbed on surfaces, including biological systems and nucleic acids. It may also be considered as a limiting case of ultrathin polymer films. The case of two dimensional athermal polymer solution is also very interesting from the point of view of polymer physics. This results from strong excluded volume interaction which leads to behavior that cannot be observed in the three dimensional case.

There was a controversy in the literature about the behavior of long chains in 2D systems. De Gennes suggested that, as the chains in 2D cannot interpenetrate, at high concentrations they should adopt disc-like conformation with

other chains being practically excluded from a surface occupied by a given coil [10]. However, computer simulations did not confirm such effect, although it should be noted that the simulated chains were not very long [2, 7, 8]. In their article, H. Meyer et al. [1] have presented static properties of a dense polymer system in two dimensions, obtained using molecular dynamics simulations. We note that the main result is that the intramolecular structure factor $F(q) = \frac{1}{N} \sum_{n,m=1}^N \langle \exp [i\vec{q} \cdot (\vec{r}_n - \vec{r}_m)] \rangle$ shows a chain length dependent slope, smaller than -2 expected for *Gaussian* chains. In the Kratky representation it reveals a strong nonmonotonous behavior. These results do not agree with theoretical predictions and are not reproduced by other simulation methods [10–14]. Carmesin and Kremer [14] (using the bond fluctuation method) obtained for very similar polymer concentration, for chains up to 100 beads slopes equal to

–2 or even bigger. As shown below also using the Cooperative Motion Algorithm (CMA) [11, 12], in Kratky representation we do not see any deviation from the Debye formula for chain of length 32–1024 in dense system, which indicates that the shape of chains does not show any deviation from the *Gaussian* shape.

II. CMA SIMULATION METHOD

We consider a two-dimensional system composed of flexible polymer chains immersed in a solvent. The solvent is essentially a monomeric solvent in which the solvent particles have a similar size to the monomers on the polymer.

In the simulations using the CMA ensembles of beads located at lattice sites are connected by non-breakable bonds to form structures representing macromolecules of various topology [11–13], all the lattice sites are occupied in order to represent dense systems like polymer melts. The presented results are obtained by simulations on a triangular lattice. The coordination number of the lattice is equal to 6, i.e. every monomer has 6 nearest neighbors.

The systems are considered under the excluded volume condition, which means that each lattice site can only be occupied by a single molecular element (chain bead or solvent particle). In such systems strictly cooperative dynamics is used, consisting in random rearrangements satisfying local continuity of the simulated system (no empty lattice sites are generated). A segment of one chain can move only if other segments of different chains move simultaneously. This is realized by local motions consisting of displacements of a certain number of molecular elements along closed loops, so that each element replaces one of its neighbors in such a way that the sum of displacements of the elements taking part in the rearrangement is zero (continuity condition). During such rearrangements the model macromolecules undergo conformational transformations, however preserving their identities given by the number and the sequences of elements in the polymer. Quantities characterizing the system are calculated only between cooperative rearrangement steps. A time step corresponds to the number of simulations steps after which an average of one attempt to move each bead was made. More details about the algorithm used are given elsewhere [11, 12]. Here we only describe simulation systems. We consider a two-dimensional system of flexible polymer chains. Simulations were performed on triangular lattice consisting of 256×256 beads for chain length $N = 32 \dots 256$ and 512×512 beads for chain lengths $N = 512, 1024$ i.e. the simulation boxes were much bigger than the average end-to-end distance of the longest simulated chains. Periodic boundary conditions were employed in all directions. In lattice simulations the polymer concentration ϕ is usually defined as the ratio of the sites occupied by the polymer beads to the total number of lattice sites. Thus $\phi = 1$ means that all the sites are occupied by the poly-

mer beads. In our case one can also define concentration in another way which will better correspond to the results obtained in [1], namely as the ratio of the sum of the surface of the circles representing polymer monomers to the total area of the regarded system. It means that the maximum concentration available corresponds to close packing of circles so it is equal to ca. 0.9069. The concentration based on this definition will be denoted by Φ .

III. RESULTS

To show that the computations performed using CMA make sense for a 2D dense system, let us check how the size of chains scales with chain length N and polymer concentration. Fig. 1 exhibits the behavior of a mean square radius of gyration $\langle R_g^2 \rangle$

$$\langle R_g^2 \rangle = \left\langle \frac{1}{N} \sum_{i=1}^N (\vec{r}_i - \vec{r}_{cm})^2 \right\rangle, \quad (1)$$

and mean squared end-to-end distance

$$\langle R_{ee}^2 \rangle = \langle (\vec{r}_1 - \vec{r}_N)^2 \rangle, \quad (2)$$

as a function of polymer concentration $\phi \geq 0.7$ for various chain lengths $N = 32, \dots, 1024$. One can observe that in all cases in the regarded region these quantities scale accordingly to the scaling prediction [5]

$$\langle R_g^2 \rangle \propto \langle R_{ee}^2 \rangle \propto \phi^{(1-2\nu)/(d\nu-1)}, \quad (3)$$

where d is the spatial dimension of the system and ν is the scaling exponent taken from the relation

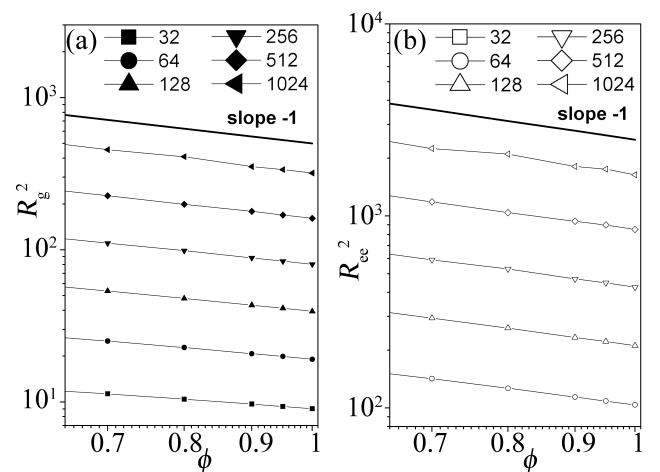


Fig. 1. Concentration dependencies of the mean square end-to-end distance R_{ee}^2 (a) and mean square radius of gyration R_g^2 (b) for various chain length plotted vs. polymer concentration $\phi \geq 0.7$. Solid lines represent slopes –1 related to scaling in dense regime

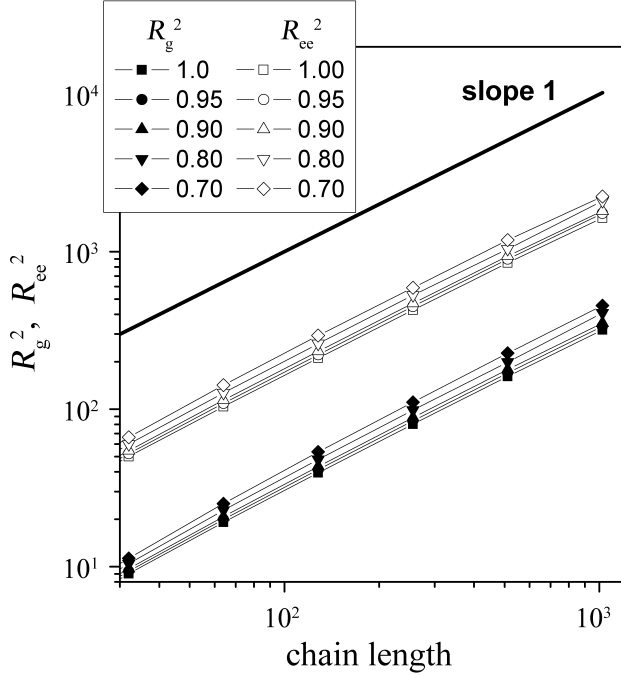


Fig. 2. Mean square end-to-end distance R_{ee}^2 (open symbols) and mean square radius of gyration R_g^2 (solid symbols) plotted vs. chain length. Dashed line indicate slope 1.0 in dense system in two dimensions as the ratio of sum of the surface of the circles representing polymer monomers to the total area of the regarded system

$$\langle R_g^2 \rangle \propto \langle R_{ee}^2 \rangle \propto N^{2\nu}. \quad (4)$$

The behavior of the end-to-end distance and the radius of gyration of chains as a function of chain length for various concentration of polymer is shown in Fig. 2. Both quantities scale in the regarded concentration range closely to $2\nu \sim 1.0$, which is a generally accepted result.

Tab. 1 shows some conformational properties for various polymer concentration in the dense regime compared with the corresponding data from [1]. Generally the results obtained by CMA are similar to the results obtained by H. Meyer et al. but asphericity and aspect ratio $\langle \lambda_1 \rangle / \langle \lambda_2 \rangle$ are slightly lower than presented in [1] for the concentration used in their simulations i.e. $7/8 = 0.875$. It suggests that in the CMA case shape of chain is more compact and more similar to a circle, but the differences seem not so drastic. Figs. 3(a) and 3(c) present unscaled structure factor $F(q)$ as a function of wave vector q for chain length $N = 32, 256$ and 1024 (for clarity we show only three curves) and concentrations $\phi = 0.95$ and $\phi = 1.0$ ($\Phi = 0.861$ and $\Phi = 0.907$) whose value is close to the concentration regarded in [1]. $F(q)$ is constant for very small wave vectors, as expected. It decreases in an intermediate wave vector range ($R_g \ll 1/q \ll 1$) and for $q \gg 1$ shows a maximum related to the lattice structure (“Bragg peak”). In contrast to the results obtained in [1] the results obtained by us

do not show any dependency on chain length in the intermediate wave vector regime. Moreover, in all cases the power-law exponent -2 (indicated by the dotted line) confirms that the statistic of chains is Gaussian and the chains exhibits behavior postulated in [2, 9, 14]. These results show that in our case the chains are self-similar, i.e. segments of long chains are packed in the same manner as those chains and the fractal dimension does not depend on chain length. Meier et al. argue in the introduction and in part III A that their chains are self-similar which, however, seems to be in contradiction with the chain length dependence observed in their Fig. 13 where the slope and thus the fractal dimension depend on chain length.

For better observation of the asymptotic power-law exponent we replotted our data from Fig. 3(a, c) in Fig. 3(b, d) using the Kratky representation (similarly like Meyer et al.)

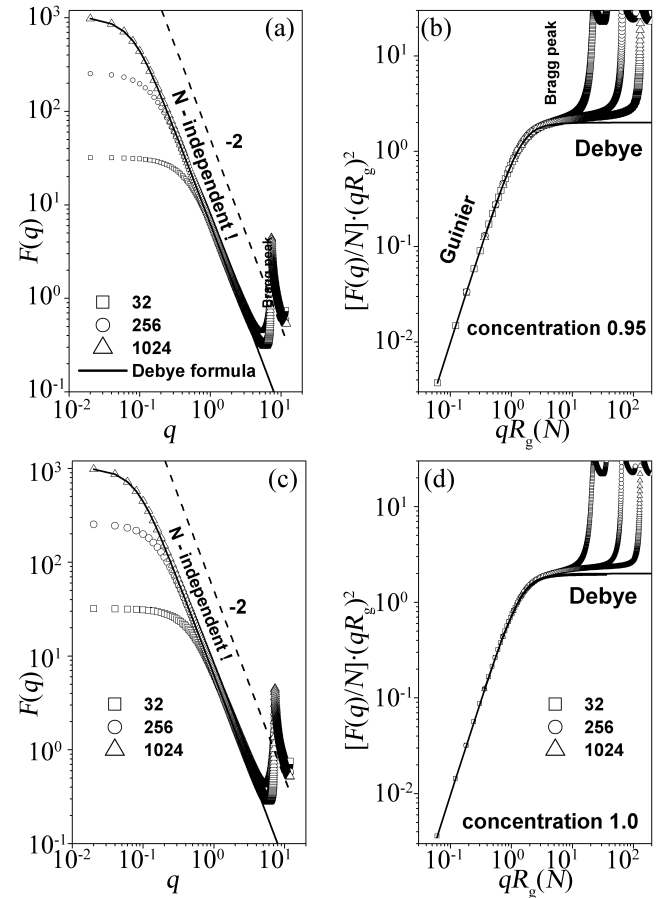


Fig. 3. (a, c) Intramolecular structure factor $F(q)$ as a function of wave vector q for different chain length as indicated. To characterize the decay in the intermediate wave vector regime our data are compared to power-law exponent -2 (dashed line). (b, d) Kratky representation of the structure factor $F(q)$ tracing $y = [F(q)/N] \cdot [qR_g(N)]^2$ as a function of reduced wave vector $qR_g(N)$ for different N using the symbols as in Fig. 3 (a, c). The Debye formula is indicated by the thick solid line. (a, b) concentration 0.95 ($\Phi = 0.861$) (c, d) concentration 1.0 ($\Phi = 0.907$)

Tab. 1. Comparison of conformational parameters for various polymer concentrations and chain lengths. The second column contains concentrations of the polymer as a fraction of lattice sites occupied by polymer beads. The third column contains concentration as fraction of the surface covered by closely packed circles representing polymer beads. The asphericity of the chains is characterized by the aspect ratio $\langle \lambda_1 \rangle / \langle \lambda_2 \rangle$ and moment Δ_2 of the eigenvalues λ_1 and λ_2 of the inertia tensor

N	ϕ	Φ	R_g	R_{ee}	R_{ee}^2/R_g^2	$\langle \lambda_1 \rangle / \langle \lambda_2 \rangle$	Δ_2
32	0.70	0.635	3.36	8.14	5.87	4.55	0.53
	0.80	0.726	3.23	7.74	5.74	4.47	0.52
	0.90	0.816	3.11	7.39	5.63	4.41	0.52
	0.95	0.861	3.06	7.23	5.59	4.39	0.52
	1.00	0.907	3.00	7.07	5.55	4.38	0.51
	Ref. [1]	0.875	3.40	8.10	5.70	4.90	0.56
64	0.70	0.635	5.02	11.92	5.65	4.58	0.53
	0.80	0.726	4.77	11.26	5.56	4.51	0.53
	0.90	0.816	4.56	10.68	5.49	4.47	0.53
	0.95	0.861	4.46	10.43	5.46	4.45	0.52
	1.00	0.907	4.37	10.19	5.43	4.43	0.52
	Ref. [1]	0.875	5.00	11.70	5.40	4.70	0.54
128	0.7	0.635	7.32	17.14	5.48	4.52	0.53
	0.8	0.726	6.92	16.14	5.44	4.49	0.53
	0.9	0.816	6.58	15.27	5.39	4.46	0.53
	0.95	0.861	6.43	14.89	5.37	4.45	0.52
	1	0.907	6.28	14.53	5.36	4.43	0.52
	Ref. [1]	0.875	7.20	16.70	5.40	4.60	0.54
256	0.7	0.635	10.52	24.31	5.34	4.42	0.52
	0.8	0.726	9.93	23.02	5.37	4.45	0.53
	0.9	0.816	9.41	21.69	5.32	4.41	0.52
	0.95	0.861	9.18	21.18	5.33	4.41	0.52
	1	0.907	8.96	20.63	5.30	4.42	0.52
	Ref. [1]	0.875	10.30	23.80	5.30	4.50	0.53
512	0.7	0.635	15.01	34.42	5.23	4.47	0.53
	0.8	0.726	14.10	32.25	5.23	4.34	0.51
	0.9	0.816	13.37	30.65	5.25	4.37	0.52
	0.95	0.861	13.02	29.96	5.20	4.40	0.52
	1	0.907	12.70	29.16	5.27	4.33	0.52
	Ref. [1]	0.875	14.70	34.00	5.30	4.50	0.53
1024	0.7	0.635	21.33	47.38	4.93	4.41	0.52
	0.8	0.726	20.22	45.82	5.13	4.45	0.52
	0.9	0.816	18.77	42.56	5.14	4.34	0.51
	0.95	0.861	18.33	41.87	5.22	4.31	0.51
	1	0.907	17.87	40.50	5.14	4.25	0.50
	Ref. [1]	0.875	20.80	48.20	5.30	4.50	0.52

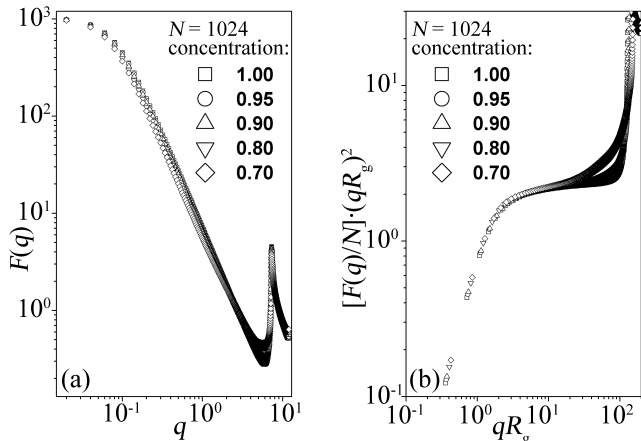


Fig. 4. (a) Intramolecular structure factor $F(q)$ as a function of wave vector q for chain length 1024 and different concentrations in dense regime as indicated. (b) Kratky representation of the structure factor $F(q)$ corresponding to Fig. 4(a)

with vertical axis $y = [F(q)/N] \cdot [qR_g(N)]^2$, using the measured radius of gyration $R_g(N)$ given in Tab. 1. We would like to underline that our results exhibit an excellent agreement with the Debye formula for *Gaussian* chains [15] (thick solid line) in all $qR_g(N)$ range below the Bragg peak. Fig. 4(a) depicts $F(q)$ and Kratky plot for chain length 1024 and various concentration ($\phi = 0.7 \dots 1.0$) of polymer in dense system. One can observe that the results obtained for various concentration are very similar. It is connected with the fact that in dense region the exponent 2ν from Eq. (4) becomes close to -1 and changes very weakly with increasing polymer concentration [16].

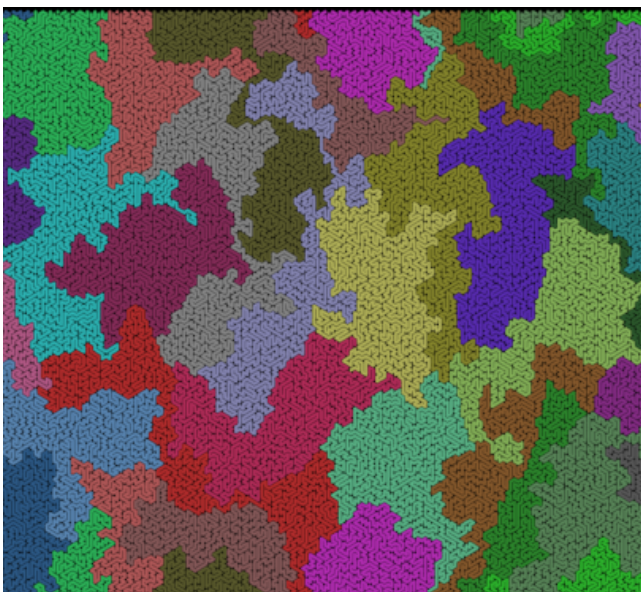


Fig. 5. A typical snapshot of the simulated system. Chain length 1024, $\phi = 1.0$ ($\Phi = 0.907$). A part of a much bigger simulation box is shown

Fig. 5 shows a typical snapshot of the simulated system. It looks very similar to Fig. 1 in [1]. It should be noted that in both images beside the compact disc-like chains we found chains which have two or more compact parts joined by a thin segment. Contribution of such chains gives significant mean asphericity in both cases.

IV. CONCLUSION

In summary, it is hard to say why simulations which yield similar values of chain size and asphericity and similar snapshots give qualitatively different predictions for scattering experiments. The arguments concerning the compact structure of scattering objects and applicability of Porod theory should apply to short and long chains and to simulations using other methods. In the future it will probably be determined by an experiment whose result obtained by us and others groups or in [1] is correct. In [1] the simulations were made for only one concentration and the system relaxation procedure may be not sufficient for the longest chains. It should be noted that the results describing the geometries of chains obtained in both cases (CMA and MD, collected in Tab. 1) are very similar. This indicates that very subtle differences in the geometry of the chain can lead to very different results in scattering factors, which may be an important indication for the people performing this kind of measurements.

References

- [1] H. Meyer, J.P. Wittmer, T. Kreer, A. Johner, J. Baschnagel, *Static Properties of Polymer Melts in Two Dimensions*, J. Chem. Phys. **132**, 184904 (2010).
- [2] A. Yethiraj, *Computer Simulation Study of Two-Dimensional Polymer Solutions*, Macromolecules **36**, 5854–5862 (2003).
- [3] C. Vlahos, M. Kosmas, *On the miscibility of chemically identical linear homopolymers of different size*, Polymer **44**, 503–507 (2003).
- [4] B. Maier, J.O. Radler, *Conformation and Self-Diffusion of Single DNA Molecules Confined to Two Dimensions*, Phys. Rev. Lett. **82**, 1911–1914 (1999).
- [5] B. Maier, J.O. Radler, *DNA on Fluid Membranes: A Model Polymer in Two Dimensions*, Macromolecules **33**, 7185–7194 (2000).
- [6] B. Maier, J.O. Radler, *Shape of Self-Avoiding Walks in Two Dimensions*, Macromolecules **34**, 5723–5724 (2001).
- [7] Y.M. Wang, I. Teraoka, *Structures and Thermodynamics of Nondilute Polymer Solutions Confined between Parallel Plates*, Macromolecules **33**, 3478–3484 (2000).
- [8] I. Teraoka, Y.M. Wang, *Crossover from Two- to Three-Dimensional Contraction of Polymer Chains in Semidilute Solutions Confined to a Narrow Slit*, Macromolecules **33**, 6901–6903 (2000).
- [9] P. Polanowski, A. Sikorski, *Universal scaling behavior of polymer chains at the percolation threshold*, Soft Matter **14**, 8249 (2018).
- [10] P.-G. De Gennes, *Scaling Concepts in Polymer Physics*, Cornell University Press, Ithaca, New York (1979).

- [11] T. Pakula, *Cooperative Relaxations in Condensed Macromolecular Systems. 1. A Model for Computer Simulation*, *Macromolecules* **20**, 679–682 (1987).
- [12] T. Pakula, S. Geyley, *Cooperative Relaxations in Condensed Macromolecular Systems. 2. Computer Simulation of Self-Diffusion of Linear Chains*, *Macromolecules* **20**, 2909–2914 (1987).
- [13] P. Polanowski, J.K. Jeszka, *Microphase Separation in Two-Dimensional Athermal Polymer Solutions on a Triangular Lattice*, *Langmuir* **23**, 8678–8680 (2007).
- [14] I. Carmesin, K. Kremer, *Static and Dynamic Properties of Two-Dimensional Polymer Melts*, *J. Phys. (France)* **51**, 915–932 (1990).
- [15] M. Doi, S.F. Edwards, *The Theory of Polymer Dynamics*, Clarendon Press, Oxford (1986).
- [16] P. Adamczyk, P. Polanowski, A. Sikorski, *Percolation in Polymer-Solvent Systems: A Monte Carlo Study*, *J. Chem. Phys.* **131**, 234901 (2009).



Piotr Polanowski received his MSc degree in Physics in 1987 from Łódź University. He earned the PhD in Chemistry from Łódź University of Technology in 2002 and the postdoctoral degree (habilitation) in Physics from the Adam Mickiewicz University in Poznań. Currently he works at Łódź University of Technology in the Department of Molecular Physics. His fields of interest cover simulations of complex molecular and macromolecular systems with saving proper dynamic behavior, parallel computing (hardware and software) in application to complex molecular systems, and simulation software development.



Jeremiasz K. Jeszka is now retired. He received his master's degree in Physics in 1972 from Łódź University, his PhD in 1978 from Łódź University of Technology and the title of Professor in Chemistry in 2008. In the years 1983–2010 he worked at the Centre of Macromolecular Science of the Polish Academy of Sciences in Łódź. His scientific interest concerns physical properties of polymers, polymer composites and interfaces. His early work was devoted mostly to manufacturing, structure-properties relationship and electrical and magnetic properties of fully organic polymer composites, so called reticulate doped polymers. Later on he worked on preparation and properties of polymer nanocomposites with metal nanoparticles and carbon nanotubes and on the effect of nanostructure and surface energy of the solid surface on crystallization of adjacent layer of polymers. He is also involved in Monte-Carlo simulations of static and dynamic properties of macromolecules and the simulations of synthesis and properties of complex macromolecules and polymer brushes. He is coauthor of 140 publications cited ca 1900 times.