



Dynamic lattice liquid (DLL) model in computer simulation of the structure and dynamics of polymer condensed systems

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Abstract: This review presents the use of Dynamic Lattice Liquid (DLL) model proposed by Pakula and coworkers. In the model polymer liquids are represented as dense systems of macromolecules. The model fulfils requirements of the local continuity and excluded volume conditions. The use of the model for numerical simulations of simple liquids, colloidal particles systems, solutions of linear polymers, branched like bottle-brush or star shaped polymers is described. The use of simulations for the prediction of the properties of the systems and their experimental validation is described. The model is presented as an universal tool for investigation of different systems that provides good agreement between numerical and experimental results for a broad range of the systems and conditions.

Introduction

Computer simulations have become recently one of the most important tools in the polymer research. They allow to inspect molecular structure and dynamics behaviour in the specified conditions. Computer simulated properties of molecules of designed structure that cannot be easily synthesized by the use of known methods, can be easily generated by computer with proper simulation algorithm. It is possible to numerically evaluate the structures and their dynamic behaviour in different external conditions. It is expected that such research will help to identify polymer structures of new and interesting properties and to direct the syntactical efforts.

Many Monte Carlo algorithms are used for simulations of static and dynamics properties of macromolecular systems on the lattice, but only few of them can be used if density coefficient $\rho=1$. Polymer chains exist mainly in a condensed form (solution, melt, glass, crystal) that inhibits their movements and correlates them with the movements of surrounding molecules. Therefore the polymer simulations require algorithms that work at density coefficient equal to unity. This density coefficient value means that every particular lattice site is occupied by the kinetic element. In such systems cooperation dynamics applies based on a rule that the movements maintain local density of a simulated system and no empty volumes in the lattice are generated. The movements are realized by local cooperative motions formed by dislocations of specified number of elements at closed loops. Any element is replaced by one of its neighbours, and the continuity condition is maintained, i.e. the amount of displacements of the elements taking part in the permutation equals to zero. During such rearrangements, the models of macromolecules are subjected to conformational changes with retention of their structural identity – the number and

the order of elements in polymer as well as topology of skeleton bonds that form macromolecule are not changed. Polymers exhibit composite structure often extended on different dimensions scale, and composite dynamics behaviour that includes relaxation in broad time scale. The novel Dynamic Lattice Liquid (DLL) model invented by Pakula [1,2] includes this requirements and allows to simulate both, single macromolecules of composite polymers as well as various polymer systems. Numerous papers has been published recently to evaluate the compatibility of this model with experimental results. The purpose of this review is to summarize the results of these reports with a particular interest paid to the possibilities of evaluation of the DLL model. The model evaluations described both, static properties (the mean squared radius of gyration, the mean squared end-to-end distance) as well as kinetic properties (the mean square displacements of chain centre of mass, the autocorrelation function of the end-to-end vector of the chains) for materials like simple supercooled liquids, polymer melts of different topology and microgels.

Method

Molecular elements in the simulations are assigned to a lattice sites and represent polymer macromolecules as beads jointed by non-breakable bonds. In the DLL model, the mechanism known as CMA (Cooperative Motion Algorithm) is applied. A single diffusion step bases on the cooperative motions mechanism of the kinetic elements and plays important role in the global relaxation process. The CMA algorithm consists of the following steps in the computer simulation:

- 1) creation of a vector field that represents the movement attempts,
- 2) elimination of inefficient movement attempts,
- 3) movement of beads along the paths of closed loops, i.e. efficient movement attempts.

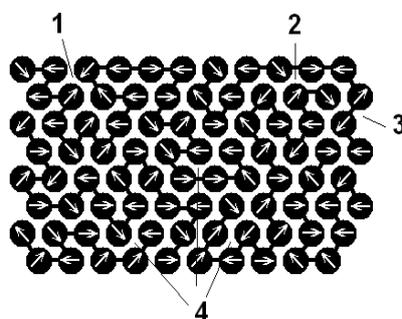


Fig. 1. Illustration of the vector field of movement attempts on a triangle lattice system that represents a polymer melt. Movement attempts 1,2,3 – unsuccessful, 4 – successful.

It is assumed that beads representing kinetic elements of a polymer, or solvent molecules, are oscillating with a specified frequency at the lattice sites. They are trying to change its position periodically towards one of the nearest neighbours. Such attempts are represented by a field of randomly chosen unit vectors that are assigned to the lattice sites and illustrate directions of the movements. An example of such assignment is shown in Fig.1 for the system that represents a polymer melt on the triangle lattice. Any vector that is not taking part in correlated movement loops fulfilling the continuity condition is eliminated. The elimination happens in the

following cases (see numbers in Fig.1): (1) two neighbouring beads are trying to relocate in reverse directions; (2) the movement attempt is starting from a lattice site toward the beads which are not attempting to move; (3) the movement would lead to breaking the bonds in the polymer chain. Cases (4) in Fig.1 illustrate successful movement attempts and are described as 3-rd step in the CMA algorithm.

The procedure described above requires a single time step of time scale τ_v . The simulation procedure is repeated during consecutive time steps and creates a set of randomly selected directions of the movement attempts. Any kinetic element can take part in only one movement attempt during a single time step to create self-avoiding loops.

A record of the coordinates of the kinetic elements after each time step is used to determine characteristic values of the structure and dynamic behaviour of the system investigated.

Structure of the modelled polymer systems can be described by the following characteristics:

- the mean square end-to-end distance of a chain composed of N beads
 $\langle R^2 \rangle = \langle (\mathbf{r}_1 - \mathbf{r}_N)^2 \rangle$ (1)
 where \mathbf{r}_1 and \mathbf{r}_N are space coordinates of the chain ends,

- the mean square radius of macromolecule gyration
 $\langle s^2 \rangle = \langle (\mathbf{r}_i - \mathbf{r}_{cm})^2 \rangle$ (2)
 where \mathbf{r}_{cm} represents space coordinates of chain's mass centre,

- static form factor

$$P(\mathbf{q}) = \sum_{ij} g(\mathbf{r}_{ij}) \frac{\sin(\mathbf{q}\mathbf{r}_{ij})}{\mathbf{q}\mathbf{r}_{ij}}$$
 (3)

where $g(\mathbf{r}_{ij}) = [c(\mathbf{r}_i) \cdot c(\mathbf{r}_j)]/N$ is site-to-site correlation function for sites separated by the vector $\mathbf{r}_{ij} = \mathbf{r}_i - \mathbf{r}_j$, and $c(\mathbf{r})$ is a contrast operator assuming values of unity for the sites occupied by the molecular elements, and zero for all other sites, \mathbf{q} – the scattering vector.

The kinetic behaviour of the modelled systems is described by the following characteristics associated with the relaxation times and diffusions:

- the autocorrelation function of bonds' orientation

$$\rho_b(t) = \frac{1}{N_b n} \sum_n \sum_i^{N_b} \mathbf{b}_i(t) \mathbf{b}_i(0)$$
 (4)

where $\mathbf{b}_i(t)$ is a unit vectors representing i-th bond orientation at time t , n - the number of chains, and N_b - the number of bonds in a chain,

- the autocorrelation function of the end-to-end vectors of the chains

$$\rho_a(t) = \frac{1}{n} \sum_i \mathbf{R}_i(t) \cdot \mathbf{R}_i(0)$$
 (5)

where $\mathbf{R}_i(t)$ - the end-to-end vector of i-th chain at time t ,

- the mean square displacements of the centre of mass of the whole macromolecule

$$\langle r_{cm}^2 \rangle(t) = \frac{1}{n} \sum_i [\mathbf{r}_{cm,i}(t) - \mathbf{r}_{cm,i}(0)]^2 \quad (6)$$

where $\mathbf{r}_{cm,i}(t)$ – time dependent coordinates of the centre of mass of i-th chain,

- the mean square displacements of a monomer molecule

$$\langle r_m^2 \rangle(t) = \frac{1}{Nn} \sum_i \sum_j [\mathbf{r}_{m,ij}(t) - \mathbf{r}_{m,ij}(0)]^2 \quad (7)$$

where $\mathbf{r}_{m,i}(t)$ - coordinates of a monomer molecule at time t ,

- the mean square displacements of a solvent molecules

$$\langle r_{sol}^2 \rangle(t) = \frac{1}{n} \sum_i [\mathbf{r}_{sol,i}(t) - \mathbf{r}_{sol,i}(0)]^2 \quad (8)$$

where $\mathbf{r}_{sol,i}(t)$ - coordinates of i-th solvent molecule at time t , n – the number of solvent molecules.

Applications

The DLL model was applied in [3] for analysis of simple liquids that freeze in a glassy form where the authors provided analytical formulae that describe the influence of the pressure and temperature on the relaxation time in the systems. In the case when the molecular displacements are controlled by the temperature and excluded volume, the description of isothermal and isobaric characteristic of structural relaxations is in agreement with the experiment results which cannot be explained neither by the Arrhenius model with constant activation energy, nor by the free volume model. The modelling of middle range order in the glassy substances was analysed in [4]. The mixtures of two types of atoms on 2D and 3D lattices at different temperatures, composition and density were also simulated. The results are in good agreement with the effects observed for inorganic glassy substances.

Dense systems of colloidal particles that are incompressible but deformable were analysed in [5]. Different structural and dynamic states covering the entire structure range, from liquid to crystalline, were depicted as a function of both, a deformability parameter and the concentration.

It is shown in [6] that the DLL model is capable to reproduce broad class of different temperature vs. relaxation time relationships, from the Arrhenius relationship to the Vogel-Fulcher-Tamman (VFT). The degrees of freedom and displacements were considered as directed by thermal activation with the energy barriers dependent on local density.

General conditions of simple liquids simulation on different lattices are presented in [7]. The interdiffusion coefficients were directly controlled by a change of the composition profiles in time. In an athermal case, the interdiffusion and self-diffusion coefficients are the same. In reacting mixtures, the interdiffusion was thermally activated.

The DLL model was proposed in [8] as a universal tool for the research on different types of aggregation. The model enables simulation of the systems of a constant number of particles and presence of a solvent molecules. Fractal growth was demonstrated in system of different initial concentrations of particles that were forming the clusters. It was shown that the fractal size increases with increasing the initial concentration. The simulation presents physically sensible structural and dynamic features of such systems.

Systematic research on athermal, linear polymer systems using 2D triangle lattice in the simulation for different concentrations and different solvents was presented in [9] where static and dynamic properties were described. The results depicted molecular packing and other properties of a single-molecular polymer layers and could be used in designing techniques of thin layer production.

The simulations of dense systems of flexible and semi-flexible chains were presented in [10]. It was noticed that the demixing transition takes place below a certain degree of chain flexibility, even without introducing the expulsion forces between the two polymers, but with excluded volume condition preserved. Phase concentrations at the equilibrium at different temperatures were calculated, as well as the phase diagrams were constructed. The results were in a qualitative agreement with the Flory lattice theory for stiff chains. The systems of stiff chains were also analysed in [11]. The chain stiffness was introduced by two methods - by limiting the deformation angles and by placing a large number of side chains anchored to the polymer backbone. The dependence of the polymer chain length on the relaxation time was analysed numerically and the results were in a good agreement with the experimental results.

Melts of the linear homopolymers were analysed under the shear stress in [12]. Simulations were done for the systems of entangled chains built of more than 640 beads and placed between two parallel walls. The behaviour of the melt under shear stress was simulated by setting up the probability of the beads movements. The chain dynamics was controlled during achievement of steady-state flow during relaxation of the melt. The results were compared with the simulation results obtained for non-flowing melts. Chain orientation, coil deformation and relaxation were also analysed. Noticeable differences were observed between step-shear and steady-states, while the dynamics of the chains during relaxation was almost identical with the non-flowing melt. Dynamics of the melt depended strongly on the chain length and shear stress, showing non-linear effects for long chains. Relaxation time for long chains decreased by orders of magnitude when affected by the shear stress creating a power-law dependence. Diffusion of beads and chains was analysed and an anomalous diffusion was observed in the flow direction as well as in the perpendicular directions. For the flowing melt, a confined space size was important, even if the wall spacing was much bigger than the radius of gyration of the polymer chains. Comparison of the linear chain systems placed between two parallel walls with the unconfined melt structure was done in [13] using the face centred cubic (fcc) lattice. The authors have shown that the effect of neutral walls consists mainly in reorientation of cigar-shaped chains in the vicinity of the walls, but the dimensions and shape of the chains were not affected. The melts composed of chains anchored by one end to one of the walls (grafted chains) were examined in [14]. The results characterizing the structure of layers, as well as the conformation and orientation of the chains were obtained for systems with various chain lengths (40, 80, and 160) and various grafting densities (0.25 and 0.5). The simulation results were compared with respective characteristics of such layers predicted by the self-consistent field (SCF) theory [15]. A good agreement with the theoretical predictions was observed, especially for longer chains and higher grafting densities, i.e. for the systems more similar to those assumed in the theory.

Solutions of diblock copolymers in various concentrations and different chain length were examined in simulations using 2D lattice [16]. Relationships between diffusion coefficients and evolution of concentration profiles were evaluated. A series of

simulations produced to evaluate the relationships between the lattice size and properties of diblock copolymer were described in [17]. For all evaluated 3D lattice sizes (30x32x30, 40x32x30, 50x32x30, 60x32x30) low temperature interfacial ordering was observed.

Analysis of triblock copolymers A-B-A in various temperatures was described in [18]. Energy, specific heat, copolymer end-to-end distance as functions of reduced temperature were calculated using CMA algorithm. Temperatures of order-disorder transitions were found on phase diagrams.

Polymer systems of complex topology, like H-shaped or star polymers were evaluated in [19]. For star polymers, the influence of number of star arms and their length on static and dynamic properties of the modelled systems was analysed in [20]. Static properties were characterized by a star size and spatial correlations. Dynamic properties described as arms orientation, relaxation and translation movement of stars were presented. The results indicate strong ordering effects for multi-arm stars in melts and suggest significant influence of arms' orientation relaxation and star translation which depend on the length and number of arms on the terminal star relaxation. Polymers of the star structure built of large number of linear homopolymer arms attached covalently to a central core can be described as a model of soft hybrid spheres that have polymer (arms) and colloid (core) character. As a result of this type of topology, single star has diversified arrangement of polymer density. In non-dilute solutions, liquid-like order appears as a consequence of growth of osmotic pressure and strong entropy-driven arm stretching appears. This type of ordering was also maintained in the melt and is caused by influence of excluded volume on molecules. As a result, rich dynamic response of the system described in [21] exhibited both, the polymer and colloid character. Relaxation of concentration and a number of density fluctuations have resulted from the cooperative diffusion, self-diffusion and structural relaxation. Final viscoelastic relaxation of the melt resulting in the arms relaxation was independent of the number of arms in the macromolecule. Structural rearrangements of the stars heavily depended on the arms number and size. Identification of the relaxation mechanisms in such a composite of soft spheres provided information necessary to design particles and control new composite materials possessing the properties of polymers and colloids.

Analysis of catenanes and comparison of their behaviour with a linear and cyclic chains simulated in the same conditions was discussed in [22]. Structural and dynamic characteristics of fused rings were shown as a function of size and number of rings. It was found that higher complexity of the catenanes architecture, in comparison with linear or cyclic chains, makes the molecular dynamics much more complex with considerable slowing down of the relaxation of whole macromolecules. The results have shown that catenanes exhibit some specific properties that cannot be found in either, linear or cyclic polymer chains.

In [23] macromolecules of bottle-brush topology under the conditions of a good solvent were investigated by the scattering methods (SAXS, SANS, SLS), as well as by the numerical simulations. Molecular architecture parameters, such as polymer backbone length, side chain length and stiffness, varied in the research systematically. Consistent description of the form factors was achieved by considering of the polymer macromolecules as flexible cylinders with a density fluctuation inside. The model leads to direct conclusions on the parameters, such as persistent brush length, describing general shape of the polymer macromolecule.

Indirect conclusions on the side-chain effect and the polymer backbone conformation were also drawn. The results were in a good agreement with the experimental data. The simulation method used gave direct access to the pairs correlation functions that allowed to find the macromolecule form factor independently. The most important parameter for liotropic behaviour of the bottle-brush polymers is the persistent length-to-diameter ratio that has a value of 10 or more. The influence of molecular architecture parameters on the stiffness of the macromolecule was also investigated and the experimental results on liotropic behaviour of polymers presented.

Non-linear highly branched polymers were investigated in [24] by low angle SAXS scattering and DMS spectroscopy, as well as by the computer simulation. The results have shown that the consequence of complex polymer topology is a specific intramolecular monomer density distribution. Polymers with complex architecture represent soft objects which order on macromolecular scale because of strong steric interactions. The simulation results are capable to represent the structure and dynamics of the considered systems.

Configurational properties of macromolecules of highly charged polyelectrolytes accompanied by neutralizing counterions in diluted solutions were simulated by the CMA algorithm using fcc lattice in [25]. The whole Coulomb potential and the influence of excluded volume between the ions was taken into consideration, and the main varied parameter was a reduced temperature T^* . Calculations made for solutions of single chains and systems of several chains distinguished several ranges of properties: (a) the case of $T^* \rightarrow \infty$ describes neutral polymers under good solvent conditions; (b) $T^* \approx 1$ corresponds to effectively stronger electrical repulsion making the chains more stretched comparing to their shape in other temperatures; (c) $T^* \ll 1$ corresponds to dominant counterions coupling leading to strong collapse of the chains structure; (d) at the lowest temperatures examined, the chains and the counterions are adopting low energy configurations as neutral aggregates.

Calculations provided in [26] showed that negative and positive ions were localized onto polymer chains at sufficiently low temperatures. Their number was function of the salt type added. As the temperatures decreased, the chains were subjected to conformational changes from neutral polymers through more stretched forms, finally reaching the conformation of wrapped spheres. The chain stretching in the middle range temperatures was influenced by the salt added. The influence of the salt valance was also analysed in two fixed temperatures in [27]. The calculations indicated that the addition of small amount of multivalent salt has a tremendous influence onto a polymer macromolecules conformation, especially in lower temperatures.

Results

One of the most analysed properties with the use of the DLL model was the molecular relaxation time (system dynamics) and the diffusion constant (static properties). A local mobility of the system was estimated basing on the site-to-site autocorrelation function. The autocorrelation function of the end-to-end vectors allowed estimation the chain relaxation time. The diffusion constants were determined based on the mean-square translation of the centre of mass or the chain segments.

Point-to-point autocorrelation functions $\rho(t)$ as functions of time were almost exponential on the semi-logarithmic graph, as shown in Fig. 2. For single beads,

possible temperature dependent intermolecular interaction and beads mobility can be introduced to the model by the term ρ that modifies a bond constant, thus changing the system dynamics [7].

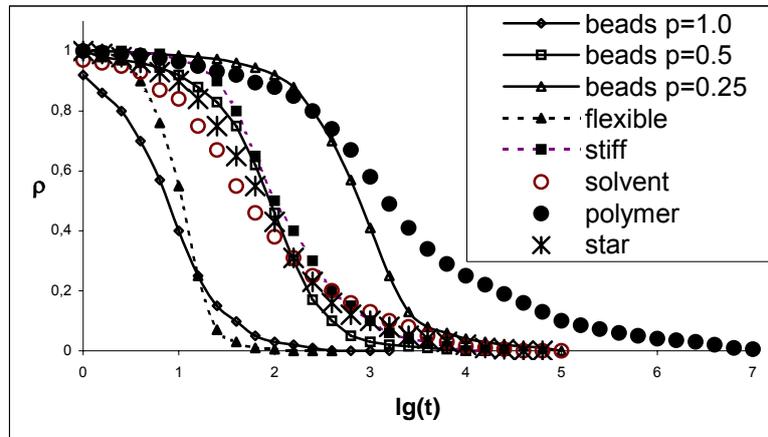


Fig. 2. Point-to-point autocorrelation functions, $\rho(t)$, vs. time. Solid lines - single beads with limited mobility [7], ($p=1$ - unlimited, $p=0.5$ - half of the lattice site available, $p=0.25$ one out of 4 positions available). Dotted lines - linear chains of $N=40$ beads and different stiffness [11]. Circles - solution of a linear polymer $N=16$, concentration $c=0.6$ (open symbols - autocorrelation function for solvent molecules, filled symbols - for polymer molecules) [16]. Stars - solution of a 24 arms star polymer; arm length: 20 beads [19-21].

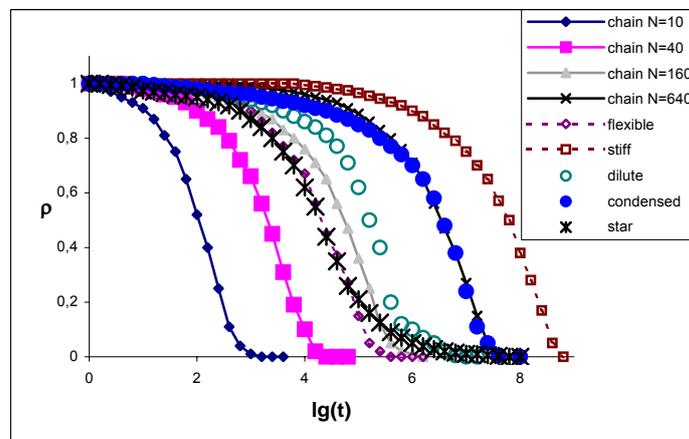


Fig. 3. The polymer end-to-end vector autocorrelation functions (for stars - centre-to-arm end vector) vs. time. Solid lines - linear chains of $N=40$ beads and various stiffness [11]. Circles - solution of $N=16$ polymer (open symbols - concentration $c=0.1$; filled symbols - $c=0.95$) [9]. Stars - star polymer solution [21].

Comparison of the influence of the accessibility parameter ρ with the results for star polymers for which local mobility was almost independent of the type and size of the molecule, as well as for the stiff polymers [11], shows a good agreement with that predicted for single beads with $\rho=0.5$ (half of the lattice sites available) (Fig. 2). Also for polymer solutions, local mobility of the solvent is close to that predicted for single beads with $\rho=0.5$, while the mobility of polymer molecules is comparable with that for

the beads with $p=0.25$. For flexible polymers local mobility is greater than for stiffness, of course.

Figure 3 shows end-to-end vector autocorrelation functions for different polymer systems. As expected, the relaxation time noticeably increased with the increase of polymer chain length [12], the influence of the chain stiffness is less important, and the polymer concentration has the least important influence [9]. The arms' relaxation for the star polymers is not considerably dependent on the arm length [21] and therefore only one example of the curve is presented in Fig. 3.

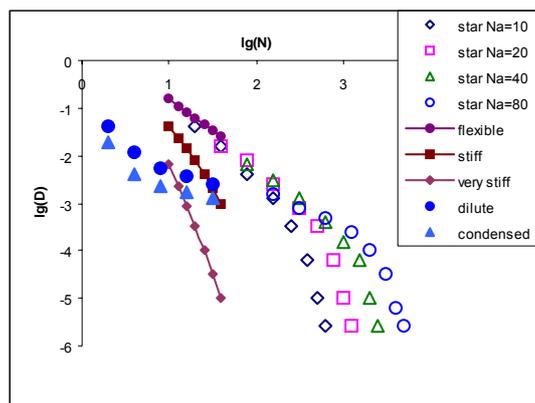


Fig. 4. Diffusion constant, D , vs. number of kinetic elements in the molecule, N . Open symbols - stars of a various arm length, N_a [20]. Solid lines - influence of the polymer stiffness [11]. Filled symbols - solutions of linear polymers of different concentration [9].

Strong changes of a global dynamics of composite macromolecular objects, like star polymers, can be achieved by variation of two parameters - arms number and length, even if the mass of the molecule remains unchanged (Fig. 4). An increase of arms number with constant arm length causes denser intramolecular packing and noticeably reduces the arm relaxation time. On the other hand, the change of the arm length, with the number of arms remaining unchanged, caused results similar to those observed for linear polymer chains [6, 20]. The polymer stiffness has also a great influence on the diffusion constant [11].

Self-diffusion constants of a monomer for each chain length weakly depends on the concentration, however it decreases sharper when the concentration becomes greater than 0.6. The reason is that in the neighbourhood of a monomer more polymer segments can be found, so the cooperative movements incorporated both, the solvent and the monomer. The dependence of self-diffusion constants of the polymer chains on the polymer concentration has a similar character for different chain lengths. Global chain dynamics in the solutions is defined by confinement of the solvent molecules between and inside the chains. Thus, for small concentrations, long-time solvent dynamics is not considerably influenced by the chain length and is similar to the local chain dynamics, due to free movement of solvent molecules between the chains. For high concentrations of the polymer, the influence of the chain length on the solvent dynamics is stronger as caused by the confinement of the solvent molecules. Therefore, in the inspected range of polymer concentrations, the dynamics of solvent molecules is defined by the polymer chains dynamics [9].

Diffusion of the chains in the flowing melt was strongly modified by the shear stress, including the displacements perpendicular to the shear direction. The diffusion of the chains' centre of mass shows an anomalous behaviour (sub- or superdiffusion) in all directions as a result of the space confinement and shear [12].

Conclusions

The DLL model represents polymer liquids as dense systems of macromolecules that fulfil the requirement of local continuity and the excluded volume condition during relocation of the beads and local density fluctuations. The model bases on the microscopic mechanism and can be applied as algorithm for simulations of a real structure in the systems from simple liquids to polymer melts. The limitations in application of the DLL model are associated with available computing power, but the model has a unique ability of parallel consideration of all system elements and is far computationally effective in comparison with other models, e.g. the molecular dynamics.

For polymer macromolecules with a composite and compact architecture, the dynamic behaviour on the macromolecular scale corresponds to the mechanism of the Cooperative Motion Algorithm in the segmental scale. It suggests that macromolecular dynamics is controlled by the same effects as in the segmental scale, i.e. by strong excluded volume interactions at dense packing and the continuity condition maintained. The CMA approach can be applied for simulations of different types of macromolecules of composite structure and should be suitable, especially for the systems with dense intermolecular packing.

Macromolecules of different topology can be represented by a lattice structure with the beads connected by non-breakable bonds in a way corresponding to the backbone contours. Structure and dynamic properties of differently branched macromolecules can be analysed vs. various parameters of the molecular structure, e.g. the arm length and number of arms for star polymers.

The simulations of polymer solutions based on the DLL model provide the results consistent with the experimental data. One of the most interesting implementations of the model is the research on the effects of polymer chain length and concentration on local and global system dynamics. It is practically impossible to obtain such information by the use of other simulation methods that base on oversimplified models, from the point of view of the computation time. Wide applicability of the model could be of fundamental importance for material engineering and allows investigation of structure and properties of materials.

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