Use of computer modeling for analysis of structure and stability of polymer solutions and colloid dispersions[*]

A.A. Markina[1], A.I. Buglakov[1], A.A. Gavrilov[1], V.A. Ivanov[1], P.V. Komarov[2,3]

[1]Moscow State University, [2]Institute of Organoelement Compounds RAS, [3]Tver State University

A great interest in the study of polymer solutions is explained by the need to develop new technologies for the creation of nanostructured materials and coatings using self-assembly methods. To realize this process, it is important to understand how the formation of nanostructured morphologies can be controlled by changing the chemical structure of the molecules and the composition of the solution. The implementation of experimental studies related to such developments requires painstaking work on the synthesis of new compounds and subsequent inspections of the resulting samples of materials. In this case, the use of virtual design with the help of computer modeling techniques allows us to first predict the properties of a wide range of model systems, and then to select from them the most suitable ones and synthesize the necessary polymers. Taking into account that in order to identify optimal conditions for self-assembling to obtain target nanostructures, it is necessary to simultaneously search through the chemical structure of the molecules entering the system and simulate sufficiently large volumes of matter, and to solve such problems, large computational efforts are required. The use of coarse-grained models and multiscale schemes can significantly reduce the simulation time. At the same time, supercomputer platforms allow modeling of molecular systems in a wide range of model parameters.

The paper discusses the development of a computational scheme based on a coarse-grained model for the method of dissipative particle dynamics [1] with the aim of calculating the structure and performing analysis of the stability of polymer solutions and colloidal dispersions, and also searching for optimal conditions for the formation of a film from aqueous solutions of polymer colloid particles stabilized by surfactants. In particular, we have developed a coarse-grained model for the aqueous solution of an acrylic copolymer and a surfactant. Controlling the behavior of the colloidal solution is regulated by chemical groups or by molecules on the surface, which have properties different from those located in the bulk phase or in solution. The stability of the colloidal dispersion depends on the degree of affinity for the solvent in which the colloidal particles are located. As an illustration of the capabilities of the computational scheme, we demonstrate our results of the influence of various parameters of the model (concentration of components, parameters of volume interaction and of electrostatic interaction) on the characteristics of the parameters of the emerging films. In the figure 1, for example, a film (a two-sided view) obtained by evaporating a solvent from a solution of an acrylic copolymer (based on methyl methacrylate, methacrylic acid and butyl acrylate) and a surfactant is shown, with the stability of the polymer micelle dispersion being evident.

Mixed micelles of polymer with uncharged surfactant tend to aggregate (as well as uncharged colloids). Systems with charged surfactant molecules can behave differently depending on the strength of the electrostatic interaction. Both with a weak electrostatic contribution and with a strong contribution, the small micelles are unstable, coagulate into micelles of larger size, and form uniform films upon solvent evaporation. If we want to stabilize the small size of micelles in the emulsion, we need to find the optimal value of charges (for example, the optimum value of added salt).

We use the method of dissipative particle dynamics (DPD) [1-2]. This method is similar to Langevin dynamics, i.e., it solves the Newton equations of motions in a system with viscous friction and random force, and the two main differences are the conservation of both the linear and angular momentum (which allows to describe hydrodynamics correctly) and using "soft" potentials (which allows to use up to ten times larger time steps in finite-difference scheme than in usual molecular dynamics, this leading to much faster evolution of a system in the phase space). A recent comprehensive review of computer simulation studies by means of DPD method can be found in Ref.

[2]. A very important modification of DPD method, which we are using in our present study, is that the electric charges on surfactant molecules and counter-ions are taken into account explicitly, and we use for electrostatic interactions the computational scheme developed in Ref. [3]. This scheme overcomes shortcomings of similar schemes for explicit charges [2]. The aim is to study the structure and to perform the analysis of stability of micelles in polymer/surfactant solutions, as well as to search for optimal conditions of a film formation from aqueous solutions of polymer micelles stabilized by surfactants. To model the film formation we apply an algorithm for evaporation of the solvent (water).
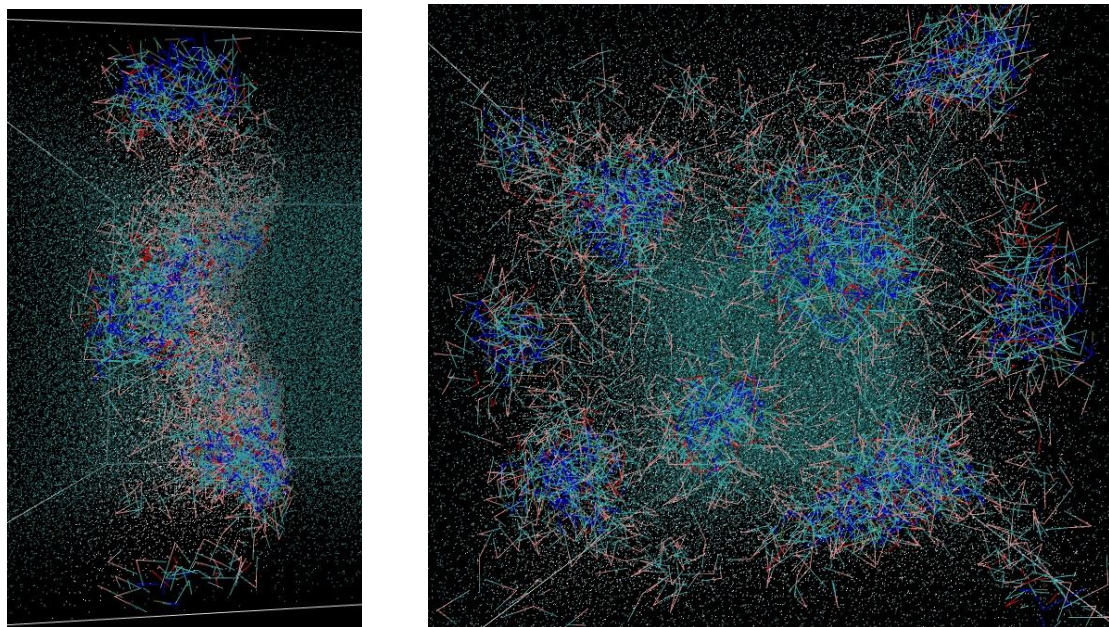

Fig. 1. A film of micelles of acrylic copolymer (based on methyl methacrylate, methacrylic acid and butyl acrylate) and surfactant stabilizing the surface of polymeric micelles (two-side view of a modeling cell).

To implement the model, we have modified our own program code DPDChem [4] for computer simulation by means of the DPD method. Different realizations of our computer code for CPU parallel computing use both the data decomposition as well as domain decomposition techniques. The use of parallel computations performed on the basis of the Supercomputer Center of Moscow State University made it possible to realize the modeling of sufficiently large cells of material during long time intervals over a wide range of selected parameters. Depending on the size of the system, the simulation was performed using 8 to 64 nodes. The choice of the number of processors was determined on the basis of the compromise in realizing the simulation of a large number of samples of the selected system (for different parameters) on large time scales (allowing to trace the self-assembly trends) and minimizing the total time expenditure due to the scalability of the program used. With a small number of processors and a system size of about 100,000 particles, the program's performance grows linearly with an increase in the number of processors up to 64 while the saturation is observed for larger number of CPU.

References

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