ФИЗИКА МЕЖФАЗНЫХ ЯВЛЕНИЙ И НАНОСИСТЕМ

TWENTY YEARS OF COMPUTER SIMULATION OF DROPLET SPREADING

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The review is devoted to the 20th anniversary of first publications on computer simulation of the droplet spreading. A special emphasis is made on the papers written by the author and his colleagues. After a short discussion of the main experimental results on macroscopic spreading and outlining the computer simulation methods, a critical review of the publications on this subject is presented. As follows from the review, the history of investigations in this field of surface science began in 1990.
Keywords: *droplet spreading, wetting, computer simulation, critical review*

1. Introduction. The present paper is a variant of my review written by an invitation of the editors of the journal "Current Opinions in Colloid and Surface Science" (Elsevier). I have added some personalities and acknowledgments to my colleagues and those who helped us at the beginning of the research.

Spreading of liquids over solid surfaces is a very interesting phenomenon from both applied and fundamental viewpoint. The wetting dynamics determines the final, i.e. static state of the droplet (the boundary conditions of wetting). The main fundamental problem relating to spreading is the obvious contradiction between the movement of the three-phase contact-line (wetting perimeter) and the no-slip boundary condition of the classical hydrodynamics. On the one hand, the droplet spreading reduces to a special case of the liquid flow being, from this point of view, a hydrodynamic phenomenon. So, it is not surprizing that basic theories of spreading are hydrodynamic [1-10]. Usually these theories are based on a solution of the Navier-Stokes equation which makes it possible to determine the velocity field in the spreading droplet and, respectively, to find all the basic spreading parameters and to investigate their time dependence. On the other hand, the spreading droplet hydrodynamics has many specific features and some questions remain open. It results in an opinion that the spreading phenomenon can not be entirely explained and interpreted in the framework of hydrodynamics. Particularly, P. de Gennes [11] used simple but interesting theoretical approach to the droplet spreading based on the nonequilibrium

71

thermodynamics. According to our point of view [12, 13], a consistent application of the nonequilibrium thermodynamics to the droplet spreading should be based on a consideration of the system of balance equations written for the bulk liquid phase, three interfacial surfaces (*sl, sg, lg*) and the linear phase, i.e. the wetting perimeter (subscripts *s*, *l* and *g* will be used to denote the solid substrate, liquid droplet and its gaseous surrounding). Unfortunately, such an approach is very difficult to be consistently developed.

In [11] P. de Gennes used a model of the spreading droplet consisting of three regions: bulk (main volume of the droplet), a quasiequilibrium precursor layer and an intermediate region between them. Later [14] P. de Gennes made a special emphasis on the role of this region in the droplet spreading. Within the region in question the Deryagin disjoining pressure plays an important role. It is also noteworthy that V. M. Starov used this droplet model in 1983 [9], i.e. earlier than P. de Gennes. The model under discussion is based on the experimental results of W. Hardy [15], who discovered the primary (precursor) layer.

Two main mechanisms were proposed to eliminate the above mentioned contradiction between the contact line motion and hydrodynamic no-slip condition. For a long time most popular was the concept of the slippage of molecules along the substrate [4-8], less popular was the rolling motion concept [16]. In his well-known review [14] P. de Gennes tried to complete the discussion on this topic making a conclusion that simple (non-polymer) liquids spread by the rolling motion mechanism whereas the polymer liquid spreading is explained by the slippage of molecules along the substrate. Most scientists have taken this point of view for granted. P. de Gennes justified his opinion referring to really remarkable experimental results of E. B. Dussan and S. H. Davis [17] (see also review [18]). These researchers photographed the motion of dye particles (marks) in the three-phase-contact line region (upper surface of the wedge) formed on solid surfaces by two immiscible fluids, including liquid-air system. As a result, they did not observe any sliding of dye particles along the solid surface. In other worlds, they observed obvious rolling motion, like to a caterpillar vehicle one, for both cases: the forced flow in capillary tubes and the spontaneous droplet spreading. These really interesting results have provoked a number of open questions. First of all, it is not clear why the slipping mechanism was not rejected by scientists just after 1974, and prestige of P. de Gennes was needed to stop the discussion on this topic. Besides, there exist experimental data on the slippage of liquids over solid surfaces in capillary tubes [19]. Probably, the rolling motion mechanism is adequate to slow enough viscous flows, and in the case of forced flows some exceptions are possible. Besides, as was mentioned in our papers [20, 21], some other open questions can be asked. Really, there is no gap between the polymer and non-polymer liquids: not only polymer molecules but also molecules of

alkanes and oligomers have the chain-like conformation. Then, if a slipping motion is really typical for polymer molecules during the spreading, it is not clear what sort of the slippage should be meant.

Obviously, the available theoretical approaches, including hydrodynamics, nonequilibrium thermodynamics and simple molecular models [22] hardly make it possible to answer the above questions. From this point of view, computer simulation methods, first of all molecular dynamics, seem to be promising to elucidate not only the laws but also mechanisms of spreading at different structural levels till observations of individual molecules and their motion. At the same time, the simulation methods themselves have some restrictions and disadvantages which will be discussed in next sections of this review. The computer simulation of spreading makes it possible to solve two groups of problems: (i) to elucidate and solve some problems of the macroscopic spreading; (ii) to investigate specific features of the nanosized droplet spreading. The last direction is of special interest in view of development of nanoscience and nanotechonology.

So, the contest and style of this review propose that it should be of interest for specialists in surface science as well as in computer simulation of other systems and processes. We do not know another review on this topic. In the available reviews on spreading [14, 18, 23], computer simulation was not discussed. In recent review [24] only computer simulation results on the dynamic contact angle formation during the forced flow in a slit-like capillary are discussed.

2. Main experimental data on the macroscopic droplet spreading. In spite of many open questions concerning mechanisms of spreading, experimental studies by E. B. Dussan and S. H. Davis [17, 18] should be treated rather as some exceptions, in a positive meaning. As a rule, experimentalists study accurately the kinetics of spreading only, i.e. dependences of the droplet parameters (first of all, geometry ones) on the spreading time t. Usually experimental and theoretical data on kinetics of spreading are presented by exponential dependences of the following type:

$$R^f - R_0^f = Bt, \tag{1}$$

where $R(t)$ is the generalized coordinate (for example, the triple-line radius in the case of radial spreading), B and f are the constants typical for each of spreading regimes, $R_0 = R(0)$ is the initial value of R corresponding to $t = 0$.

In most works the spontaneous spreading of a small droplet on the solid surface has been studied. A loose condition for getting rid of the gravitation is the smallness of the capillary length $(\rho g / \sigma)^{-1/2}$ in comparison with the droplet dimensions, where ρ is the density of liquid, σ is the

surface tension and g is the gravitational acceleration. For small drops one may assume that $R_0 = 0$ and, therefore,

$$R = At^n, \qquad (n = f^{-1}, A = B^n),\qquad (2)$$

where A and n are some redefined constants. It is assumed that each value of n corresponds to a definite spreading regime. Obviously, the spreading regime should be associated with a main mechanism of the process, in its turn relating to the resistance to the spreading process. The initial and very quick ($10^{-3}\ldots10^{-2}$ s) regime of spreading is referred to as kinetic and the following one as hydrodynamic. In turn, regarding to the main hydrodynamic factor (inertial effects or viscous flow) two forms of the hydrodynamic regime are possible, i.e. inertial and viscous. Being most prolonged and important from the practical point of view, the viscous regime has been investigated more thoroughly for various liquids (organic substances, water, polymers, metals, oxides) on various solids. The experimental data on this topic are presented and analyzed in review [25]. In many cases, the power dependence $R = At^{0.1}$ has been predicted theoretically and confirmed by experimental data, e.g. for water on glass [26] and silicon oils on glass [27]. In most available reviews and papers, the cases of complete and incomplete wetting are not thoroughly differentiated. The spreading kinetics is characterized, first of all, by the value of the exponent n as well as the exponent m in the dependence of the pre-exponential factor A on the droplet volume V ($A \sim V^m$) or the droplet mass M ($Q \sim M^m$). Experimental and theoretical results of Rehbinder's school on the topic under discussion are summarized in Table (see references in [13]).

Likely to computer simulation methods to be discussed below, methods of similarity and dimensionalities take an intermediate place between theoretical and experimental methods. The first are referred to as the mathematical simulation, the second as the physical one. The similarity methods make it possible to distribute results of a separate laboratory experiment to a whole class of similar objects or phenomena. In [13, 30] methods of similarity and dimensionalities were applied, for the first time, to investigate the droplet spreading kinetics. For viscous spreading in the cases of complete and incomplete wetting the relationship

$$m = (1 - n)/3\qquad (3)$$

between the exponents n and m was obtained. For the spreading of large droplets under the gravity effect the relationship between p and n should be written as

$$m = (1 + n)/3\qquad (4)$$

In the last column of the Table, the values of m are presented calculated using formulas (3) and (4). Experimental data on n were taken from the second column of Table. One can see that the values of m predicted by the similarity method agree with the values found experimentally.

T a b l e . Main experimental data of Rhebinder's school on the spreading kinetics

Type of wetting	Experiment		Theory		m (similarity theory)
	n	m	n	m	
Complete					
Small drops (radial) [a]	0.23…0.26	0.25	0.25	0.25	0.26…0.25
Small drops (radial) [b]	0.30…0.35	0.3	0.33	0.33	
Large drops (radial) [c]	0.12…0.15	0.35…0.40	0.13	0.39	0.37…0.38
Incomplete					
Small drops (radial) [d]	0.10…0.12	0.3	0.1	0.3	0.3…0.29

[a] These data relate to the spreading of small mercury droplets ($M < 20$ mg) on solid metals (e.g. zinc, cadmium, tin, lead, indium). Later is was found [28] that viscous regime of spreading of pentadecane, dodecane and dodecane vaseline oil mixtures on steel can be separated into two successive stages with $n = 0.25$ and $n = 0.1$. The results concerning spreading of polymer liquids are not quite consistent. Particularly, according to one of the most accurate experimental studies performed by Tanner [27] for silicon oils on glass, $n = 0.105$. At the same time, for PDMS on mica (which also is wetted completely) the value $n = 0.28$ was experimentally observed [28].

[b] In these experiments a long narrow 'path' was prepared on a metal surface (the neighboring parts were covered with an unwetted dye). It was found that the spreading kinetics could also be described with the power function $R = At^n$, where r is the distance between the drop centre and the triple line.

[c] For large drops ($M > 20$ mg), two successive stages of spreading can be identified. They are both described by the function $R = At^n$. At the first stage the exponent $n = 0.12...0.15$, and the coefficient $A \sim M^{0.35-0.40}$. Later, at the second stage, $n = 0.22...0.26$ and $A \sim M^{0.25}$.

[d] The kinetics of spreading in the case of incomplete wetting was investigated for liquids with relatively high viscosity (solutions of metals in mercury or indium, for example). A similar correlation, $r = At^{0.1}$, can also be deduced for the spreading of other viscous liquids, for example, glycerol and liquid polymers on Teflon, aluminum and mica [29]. Marmur [25] has summarized that in most cases $n = 0.1...0.15$ and $p = 0.3...0.36$ not differentiating, however, the cases of complete and incomplete wetting.

3. Computer simulation methods. As was mentioned above, computer simulation methods take an intermediate position between theory and experiment. For this reason, they are often called 'computer experiments'. We believe that these methods are really closer to usual, i.e. laboratory experiments in stating problems, obtaining and analyzing results. During computer simulation, the researcher creates modeling virtual world using for this purpose a computer program. If the laws of the virtual world are adequate, it will be similar, to a greater or lesser extent, to the real, i.e. simulated system. Otherwise, some artificial results (artifacts) are possible. Of course, any simulation is a caricature of the real system. However, a talented cartoon can reproduce some essential features of a hero, even better than a photo or a documental film.

In the atomic (large scale) simulation we do not take into account (at least directly) the electronic structure of atoms and molecules. So, the atomic size, intermolecular forces and some special effects (for example, angular dependence of interactions) are described by means of interatomic (intermolecular) potentials, including pair and many body ones. During last decade so-called *ab initio* methods become more and more popular. These methods correspond to a distribution of the quantum chemistry methods, applied before for molecules, to clusters and other nanosized systems. *Ab initio* simulation, or so-called simulation from 'first principles', makes it possible to investigate the system evolution at an electronic level. However, much more computer resources are needed for this. As a result, they can be applied, as a rule, to clusters containing of order of 100 atoms only. Besides, the results of these methods are not always reliable, i.e. some artifacts are also possible. However, we believe that in the future *ab initio* methods will be successfully applied, particularly combining with the atomic simulation. Particularly, interatomic interaction potentials may be derived from *ab initio* calculations. *Ab initio* methods can be also combined with Monte-Carlo and molecular dynamics [31].

In this paper computer simulation at the atomic level will be discussed as *ab initio* methods hardly have been applied to study the spreading dynamics. All the computer simulation methods may be divided into two classes: (i) probabilistic approaches (Monte-Carlo methods) and deterministic methods including molecular dynamics. Monte-Carlo methods, being probabilistic, propose some manipulations with pseudo-random numbers generated by special algorithms and procedures. Monte-Carlo simulation of system composed of atoms or molecules is based on the next algorithm. For each chosen atom, i.e. for i-th one, a small but arbitrary displacement $\Delta \mathbf{r} = \{\Delta x_i, \Delta y_i, \Delta z_i\}$ attributed defined by three pseudo-random numbers ξ_x, ξ_y and $\xi_z \in [0,1]$. For example, $\Delta x_i = a \cdot (2\xi_x - 1)$, where a is the amplitude of the displacement. If the potential energy u_i of this atom (in the force field

of its neighbors) is less than the initial value u_{i0}, the new position of the atom in question will be adopted. Otherwise, a new position may be also accepted but with a probability. For this purpose, different algorithms were proposed. The most known is the Metropolis scheme. In accordance with this algorithm, another random number $\xi \in [0,1]$ is chosen. If $\xi < \exp\left[-(u_i - u_{i0})/kT\right]$, the i-th atom is rest in its new position. Otherwise, it returns in the initial position. As one can see, Monte-Carlo does not deal with real trajectories of atoms and their velocities, with the exception of some artificial and rarely used variants [32]. In other words, Monte-Carlo does not correspond to simulation in the real time. If a dynamic process, e.g. spreading, is simulated by Monte-Carlo, it is assumed that the time is proportional to the number of steps of the system evolution.

Molecular dynamics (MD) is the most popular and widely used simulation method. Classical, i.e. atomic molecular dynamics is based on the solution of the system of Newtonian equations for all the atoms the simulated system consists of. For this purpose, the internal and external forces acting on each atom should be known. These forces are calculated using a potential of the interatomic interaction: a pair potential $\Phi\left(r_{ij}\right)$, a uniparticle potential $u_i(\mathbf{r_i})$ or a many body one. Contrary to Monte-Carlo, MD corresponds to simulation in the real time. In other words, the time t can be easily found for each state of the evolving system if its parameters are known. Usually, for correct numerical solution of Newtonean equations, a very small time step of the order of (1...10) fs should be chosen. So, a characteristic time scale of the processes, simulated by molecular dynamics is of order of $1\,\mathrm{ps} = 10^{-12}\mathrm{s}$. If a standard modern personal computer is used, the duration of the simulated process can be increased up to $1\,\mathrm{ns} = 10^{-9}\mathrm{s}$. Usually it is enough to understand the system behavior at the nanoscale size level.

In spite of the simple idea of MD method, many difficulties should be overcome for its development as a method of scientific research. It is also worth to mention that there exist two basic versions of the atomic molecular dynamics. The adiabatic one is most close to the classical Newtonian mechanics and proposes that the energy of the system $E = E_{kin} + U = \mathrm{const}$ (E_{kin} is the kinetic energy, $U = \sum_i u_i$ is the potential part of the internal energy E). The temperature T is not figuring in the adiabatic MD algorithm. If a big molecule, e.g. a protein one, is simulated by such a method, a heat perturbation (kink) will walk from one part of the molecule to another up to the infinity. Most of real systems do not behave themselves like this. For example, if we shall try to simulate the droplet spreading by the adiabatic molecular dynamics, the droplet temperature will crucially grow because of the evolving of the heat of wetting. So, the adiabatic MD is very rarely used

contrary to the isothermal MD which proposes a temperature control during the simulation procedure. In principle, all the components v_i of the velocities of all the atoms can be slightly cut off to adjust the kinetic temperature $T_{kin} = (2/3)k^{-1}\sum_{i=1}^{3N} M_i v_i^2/2$ (k is the Boltzmann constant) to the given thermodynamic temperature T as desribed in [33]. However, such a rough interference into the system evolution prescribed by Newtonian equations will disturb the realistic phase trajectory of the simulated system. As a result, some artifacts may be observed. For example, at the early period of our studies of the spreading simulation, we obtained nanocrystals instead of droplets at temperatures higher than the macroscopic melting temperature. For these reasons, the rough velocity rescaling is not used in professional MD research. Instead of this, some special thoroughly elaborated and justified algorithms are used called thermostats: some of them imitate a real thermostat, the other reproduce its role via some formal ways [32].

The main limitations of all atomistic computer simulations are (*i*) the limitation on the number of atoms N in the simulated system; (*ii*) that on the time duration *t*. Even supercomputers can not simulate macroscopic system containing an order of 10^{23} atoms. Usually $N < 10^5...10^6$ are available for the atomic simulation.

So, only nanosized systems are suitable for the application of computer simulation methods. Besides, systems having the infinite extension in 2 or 3 dimensions can be also simulated using so-called periodic boundary condition. For this purpose a cell (usually cubic) is chosen inside a bulk phase or a film. Then this cell is translated (reflected) in all directions to be entirely surrounded by its copies. Such a trick makes it possible to imitate an infinite medium or an infinite film. The bigger is the basic cell, the more correct will be the simulation results. At any rate, periodic boundary conditions promote some additional artificial ordering in the simulated object. A spreading droplet can not be divided into separate cells. At the same time, periodic boundary conditions are also used at the droplet spreading simulation but in another manner. For example, in [34] the whole cell, containing the droplet, 'reflected' in its surrounding. So, there will be 24 twins of the basic cell, their number corresponds to the whole number of faces, edges and vertices of the cube.

In our first molecular dynamic experiments on the droplet spreading we used a cell in the form of a hemisphere for an initial configuration corresponding to a spherical droplet located above the center of the cell base. The size of the cell is chosen under condition that the droplet could spread completely up to the formation of a disk-like monolayer. For the simulation of the disk-like droplet evolution, the cell was of a cylinder form. The whole system droplet-vapor corresponds to a closed thermodynamic system model. If the cell size is much higher than the droplet size, a noticeable part of

molecules will be evaporated to form the vapor phase. In the opposite case of a small cell when the gap between the droplet meniscus and the wall is of order of the pair potential cut-off radius, the reflection of molecules from the wall can result in deviations from the momentum or angular momentum conservation laws. In other words, the droplet as a whole will 'walk' along the substrate or rotate. To prevent these artificial effects we have used toroidal boundary conditions imitating the location of the droplet in an infinite vapor medium.

So, the main idea of computer simulation methods is simple enough and clear. However, a professional application of these methods as instruments of the scientific research is possible under thorough analysis of many factors which can yield some artifacts of simulation.

4. Computer simulation of the droplet spreading. Analyzing publications on the computer simulation of spreading, we shall follow the chronological principle with the exception of our papers. Obviously, first papers on the computer simulation of spreading were published in 1977 by E. D. Shchukin and V. S. Yushchenko [35, 36] (ten years later the same results and the same figures, as in [35, 36], were presented in English language paper [37]). These authors applied molecular dynamics to very small circular 2D-clusters containing 19 atoms only. In spite of this, the evolution of these 2D droplets in the force field of a 2D–substrate really reminded the droplet spreading. At the time under discussion, computer graphics was not developed. So, to present the simulation result, E. D. Shchukin and V. S. Yushchenko used a sort of furniture nails. On a screen, heads of these nails presented atoms. Step by step a cartoon was made demonstrating the 2D–droplet spreading.

It seems that no papers on computer simulation of spreading were published for next more than 10 years, i.e. up to the end of the 80ths. We believe that interest to the computer simulation of spreading in 90ths was stimulated by interesting laboratory experiments of A. M. Cazabate *et al.* [38, 39]. In these ellipsometry experiments spreading of quasi-flat (disk-like) droplets of polydimethil-siloxanes (PDMS) and squalane was investigated. These droplets were nanosized in their height only (of order of 10 nm) and formed on silicon wafers with an injector. PDMS are silicon oils, i.e. oligomers with very low degree of polymerization $p < 20$. One of the main features of PDMS which seems to be principal in some wetting phenomena, is that they are practically non-volatile. So, it can be expected that the droplet evaporation and recondensation of atoms before the triple-line can not disturb the wetting processes. The most important results emphasized in [38, 39] are the following: (*i*) the spreading droplet has a terrace-like (step-like) morphology (the phenomenon of dynamical layering); (*ii*) the wetted area radius R follows the diffusive law

$$R \sim \sqrt{t} \,. \tag{5}$$

Obviously, the year of 1990 should be considered as the beginning of the modern stage of the computer simulation of spreading. In [39] not only laboratory experiments but also some Monte-Carlo results on the droplet radius $R(t)$ were presented. These results demonstrate two diffusive regimes ($R \sim \sqrt{t}$) with different values of the proportionality coefficient. Unfortunately, these Monte-Carlo results were obtained using a not quite clear algorithm. Besides, they correspond to the $R \sim t^{1/4}$ law rather than to two different diffusive laws. Some of our Monte-Carlo and molecular dynamics studies of the primary spherical droplets spreading containing 240 [40], 600 and 1000 atoms [41] also demonstrated two diffusive spreading regimes. My co-author, S. D. Muravyev was a 13 years boy when we started our investigations on the computer simulation of spreading within the framework Soros foundations grant program. Unfortunately, having more than 30 publications satisfying the requirements for the PhD thesis this talented and capable student suspended his scientific activity like many other young Russian researchers.

Particularly, two diffusive regimes were observed [42] at the spreading of droplets consisting of $N = 1000$ interacting centers and $N/p = 100$ chain-like molecules (in the case under consideration $p = 10$). Other distinctive features of this system are as follows: (*i*) the equilibrium value of the variance angle $\alpha_e = 120°$ corresponds approximately to aliphatic chains, (*ii*) the chosen value $\varepsilon_s^* = 50$ of the reduced energetic parameter of the substrate ε_s^* is high enough. We consider such a substrate as a super-high energy one [42] (the meaning of the ε_s^* parameter will be explained below). In [39] it was noticed that the increasing of the substrate energy promotes the effect of the dynamical layering. Probably, the second diffusive regime also relates to the high-energy nature of the substrate. In our later works [20, 21], where larger droplet was simulated ($N = 3000$), the second diffusion regime of spreading was not observed. At the same time, the regime $R \sim \sqrt{t}$ has been revealed very often. However, deviations from this law were also observed.

In our works on computer simulation of spreading and in most other papers, usually Lennard-Jones droplets are simulated, i.e. droplets consisting of atoms interacting in accordance with the Lennard-Jones pair potential

$$\Phi(r) = 4\varepsilon \left[\left(\frac{a}{r} \right)^{12} - \left(\frac{a}{r} \right)^{6} \right], \tag{6}$$

where r is the interatomic distance, ε is the energetic parameter of the pair potential (the potential well depth), a is a linear parameter interpreted as a characteristic atomic diameter. This parameter plays the role of a linear scale at the spreading simulation, whereas ε is figuring in the definition of the reduced temperature $T^* = kT / \varepsilon$. Potential (6) should ideally describe molecular systems with spherical molecules. Chain-like molecules, reproducing polymer molecules to a greater or lesser extent, are usually simulated by short enough chains consisting of interacting Lennard-Jones centers. Chemical interactions can be described by the parabolic potential $U_r(r) = K_r(r - r_0)^2$, where r_0 is the equilibrium value of the bond length, and K_r is a constant of the bond rigidity. The oscillations of the valence angle α can be taken into account in a similar way. It is also worth to mention that short modeling chains allow two different interpretations. On the one hand, a direct interpretation proposes that each interacting center reproduces a small enough fragment of a molecule like n-alkanes and oligomers, including PDMS. On the other hand, each segment of the modeling chain may be interpreted as the Kuhn segment of a real more or less flexible polymer chain with the degree of polymerization p much higher than the modeling chain length.

The solid surface (substrate) can be described in a continual approximation. For example, it can be taken into account by integrating the Lennard-Jones potential over the half-space occupied to the solid. Besides, a discrete treatment can be used when some number of atomic layers of the substrate are directly taken into account. Let us denote by ε_l the energetic parameter of the pair potential for the droplet–vapor subsystem, and by ε_s for the solid substrate. So, the parameter $\varepsilon_s^* = \varepsilon_s / \varepsilon_l$ characterizes the relative energy of the substrate. As was shown in [40], the values $\varepsilon_s^* \leq 2$ correspond to low energy substrates [43], and the range $\varepsilon_s^* > 2$ to high-energy ones.

Another problem of the droplet spreading simulation, which is also worth to be discussed, concerns the definition of the wetted area radius R. The problem is that the nanodroplet edge is not always well differentiated. Besides, the wetting perimeter of nanodroplets is not always circular. Moreover, the first (lower) monolayer is frequently represented by a set of two-dimensional clusters (islands), thus making the problem even more complicated. However, as was mentioned in section 2, the $R(t)$ dependence may be treated as the main way of the presentation of results on the droplets spreading. For this reason, $R(t)$ dependence was widely used in most papers on spreading simulation. Usually, the first monolayer radius $R_1(t)$ is interpreted as the triple line radius $R(t)$ though the problem of its correct and programming determination is not trivial. In [44] the linear boundary of the

lower monolayer was determined as the coordinate of an abrupt decrease in the radial density distribution function. A similar algorithm was used in our computer program developed by the author and V. V. Dronnikov. The base of the modeling cell is divided into eight sectors by four normal cross-sections. The boundary of the droplet base corresponds to the coordinates of the abrupt decrease in the radial density distribution function. Thus, we may obtain four kinetic curves for the sizes of the wetted surface area in the directions of different cross-sections of the droplet. Then, by averaging these results, the kinetic dependence is obtained for the radius R_1 of the wetted surface area. To compare with the method used in [44], our approach enables us to avoid further processing in the cases when the sizes of the wetted regions vary greatly in different directions.

This year corresponds to the 20th anniversary of the first meaningful publications on the molecular dynamics of spreading. The papers on molecular dynamics of spreading may be conditionally divided into two groups. The first one corresponds to basic systems, i.e. simple or polymer nanodroplet spreading over homogeneous substrates (continual or with an atomic structure). The second group, corresponding to special cases of spreading, will be treated later. In [45] the Lennard-Jones nanodroplet spreading was simulated by molecular dynamics. The droplet consisted of 4000 atoms. The authors insisted that they observed the terraced wetting though such an effect was not pronounced. Of course, droplets under consideration had layered structure, determined by the flat geometry of the solid surface. Nonuniformity of the density along the normal to the substrate plane was observed in many later works including ours. It is also noteworthy that in [45] the linear dependence of R_1^2 on $\log(t)$ was observed which does not agree neither with experiments of A. M. Kazabat et al [38, 39] nor with the following papers on computer simulation on spreading.

In [34] spreading of Lennard-Jones nanodroplets containing 780-2860 atoms was simulated. The substrate was assumed to be homogeneous (continuous), i.e. without atomic structure. It seems that the case of partial wetting was investigated (the energy of the substrate is not clearly given in paper [34]). According to the abstract of [34], the authors simulated the spreading of nonvolatile liquid droplets. Respectively, no vapor molecules are seen on snapshots presented in the paper. However, it is not correct, especially for a high enough reduced temperature $T^* = 0.8$, as the simple Lennard-Jones fluid can not be entirely nonvolatile. For the reduced temperature $T^* = 0.57$ (this value is closer to the triple point of the Lennard-Jones fluid), the linear dependence of the wetted area w on time t, i.e. the diffusion law $R_1 \sim \sqrt{t}$ for the first monolayer radius R_1, was observed. For $T^* = 0.8$ a crossover from a regime with practically constant speed (i.e. $R_1 \sim t$) to the diffusion law ($R_1 \sim \sqrt{t}$) was observed. However, the $w(t)$

dependence is sooner a continuous function corresponding to $w \sim \sqrt{t}$, i.e. $R_1 \sim t^{1/4}$.

In similar papers [46, 47] molecular dynamics was applied to the spreading for droplets presented by monomer (solvent)-dimer and monomer-tetramer mixtures. For monomer-dimmer systems stepped droplet shape was observed. For monomer-tetramer droplets layering occurs in the case of relatively strong surface potentials. On low energy substrates droplets had rounded shape. Some interesting orientation effects can be also discussed: chain-like molecules can have homeotropic orientation, i.e. be perpendicular to the substrate like a hair standing on the end. Something like this was observed in our computer experiments [42]. The dependences $w(t)$ presented in [47] are not linear and seem to be described by the law $w \sim \sqrt{t}$ ($R_1 \sim t^{1/4}$). We should also note that in [46, 47] evaporated molecules of monomers are also not seen in the figures. In [48], using molecular dynamics simulation, the spreading was investigated of droplets consisting of octamers ($p = 8, N = 2048$). As a result, ideally linear dependences of R_1^2 on t were obtained. In [49] the case when $p = 16$ was examined.

After 1995 the flow of publications on the computer simulation of spreading seems to be ceased. Paper [50] should be noted in which the spreading of large enough droplets of the simple Lennard-Jones fluid, consisting of 40000 monatomic molecules, was simulated. A distinctive feature of this work, in comparison with previous ones, is that the authors investigated the wetting dynamics, i.e. the dependence of the dynamic contact angle θ on the spreading time t. Paper [46] may be treated as one of the most accurate investigations of the droplet spreading. In this work, most large modeling droplets were simulated consisting of 200000 monomers from which modeling chance were constructed as was explained above (in [44] such a chain was referred to as the bead-spring model). The chains in question had lengths corresponding to 10, 20, and 40 monomers. To study the dynamics of both the precursor foot and the bulk droplet, large hemispherical initial configurations were used. The authors compared spreading on flat continual and atomistic surfaces. It is also noteworthy that in [44] two different thermostats were used based on the Langevin and dissipative particle dynamics to compare results corresponding to different ways of the temperature control. It was found that the type of thermostat (being adequately applied) as well as the choice of the continual or atomistic (discrete) substrate do not change principally the kinetics of spreading: the authors of [44] observed the diffusive behavior for the precursor foot ($R_1 \sim \sqrt{t}$) that is in agreement with other molecular dynamics results discussed in this review as well as with experimental results [38, 39]. The authors of [44] aimed to reach a hydrodynamic behavior of the spreading droplet, i.e. the spreading kinetic typical for macroscopic droplets (sec. 2).

However, despite large enough simulated systems, hydrodynamic behavior was not observed.

The above discussion demonstrates that kinetics and mechanisms of the droplet spreading (including macroscopic and nanosized systems) are not entirely clear. Particularly, different time dependences for the first monolayer (the precursor foot) R_1 were observed in different works on computer simulation of spreading. For this reason, in [21], we studied accurately the spreading kinetics for droplets of the simple Lennard-Jones fluid and droplets consisting of modeling chain-like molecules. Contrary to [44] we dealt with much smaller nanodroplets consisting of 3000 monomers (single or combined into chains). We found that the diffusion law $R_1 \sim \sqrt{t}$ really is often observed but as an approximation. At the same time, many deviations from this law take place. Particularly, the exponent n is very close to 0.5 ($n = 0.48$) in the case of simple nanodroplets spreading over the low-energy substrate characterized by $\varepsilon_s^* = 1$ ($T^* = 0.65$). The spreading of analogous droplets over the high energy substrate with the energetic parameter $\varepsilon_s^* = 5$ is ideally described by the law $R_1 \sim t^{0.6}$. During the last year we have simulated the wetting dynamics for droplets consisting of 40000 atoms (these results, presented in Fig.1 and 2, have not been published yet). One can see that practically the same law $R_1 \sim t^{0.61}$ is observed. In [21] we showed that diffusive law $R_1 \sim \sqrt{t}$ really corresponds to the surface diffusion of atoms along the substrate, i.e. the nanodroplet spreading rate is of order of the rate of the surface diffusion. However, the diffusive law should be ideally fulfilled for the ideal case of the surface diffusion from an unlimited source. From this point of view, deviations from the law in question are explained by a deviation from the ideal surface diffusion process. In [20] a comparative molecular dynamics study of the simple and polymer nanodroplets spreading was performed to elucidate the spreading mechanism. A conclusion was made that the spreading of simple fluids rather corresponds to the rolling motion mechanism (to a less or greater extent) whereas modeling polymer droplets spread following to the slippage mechanism. However, a very special sort of slippage is meant, i.e. the chain reptation along the substrate in the direction of spreading. It is also noteworthy that in the bulk polymer physics reptation corresponds to a worm-like motion of very long chains in an imaginary tube formed by neighboring chains [51]. So, the reptations during the polymer droplet spreading should differ from those in the bulk polymer phase.

There is an interesting problem concerning the nanodroplet spreading and practically not discussed in the literature. We mean the dependence of kinetics and mechanisms of spreading on the droplet geometry.

F i g . 1. Snapshots of a droplet consisting of 42000 atoms on the high-energy continual substrate ($\varepsilon_s = 5$, $T^* = 0.6$): (*a*) lateral view of the initial configuration, (*b*) intermediate configuration, (*c*) final (equilibrium) state corresponding to complete wetting.
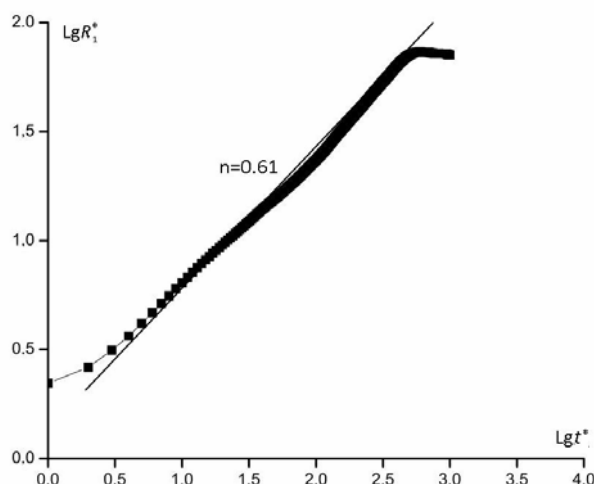
F i g . 2. The dependence of $\lg R_1^*$ on $\lg t^*$ obtained using results of three series of computer experiments for the case when $N = 42000$, $\varepsilon_s = 5$, $T^* = 0.6$

Really, laboratory experiments [38, 39] were performed for very thin disk-like droplets whereas most computer experiments have dealt with the initially spherical droplet geometry. Though in [38, 39] the diffusive law $R_1 \sim \sqrt{t}$ is proposed to be held for any droplet geometry, it is of interest to compare the spreading of spherical and disk-like droplets. In the 90ths we prepared a paper on the disk-like droplet spreading simulation for 'Colloid Journal'. In this paper some distinctive features of disk-like droplets were emphasized. The reviewer of the paper in question was Chief-editor of the journal Prof. N. V. Churaev. He gave a warm enough review but remarked that the kinetics of the final stage of spreading and, especially, the equilibrium state of the droplet should not depend on its initial form. Unfortunately, at that time we did not publish an improved manuscript. It seems that for the first time the problem under discussion was investigated in [52], where the spreading of one- and two-component disk-like polymer nanodroplets was studied using MD. The droplets consisted of chains of length 10, 40, and 100 monomers. Each droplet contains about 350000 monomers. The dynamics of the individual components of each droplet was analyzed and compared to the dynamics of single-component droplets for the spreading rates of the precursor foot and bulk droplet, the time evolution of the contact angle, and the velocity distribution inside the droplet.

It was found that the precursor foot grew diffusively in both cases. The contact angle θ was diminishing from 80º to approximately 20º also in both cases. So, in general, the opinion of N. V. Churaev was really justified

by these computer simulation results. However, it is not clear why $\theta_e > 20°$ for the cylindrical geometry and $\theta_e < 20°$ for the spherical one.

After the 90ths most of the papers on computer simulation of spreading were published with participation of J. De Coninck [53-58]. Detailed analysis of these works is beyond the scope of the present review. According to the title of the last paper [58] published in 2010, the authors present new evidence for the microscopic validity of the molecular-kinetic theory of spreading using the large-scale molecular dynamics. As for molecular-kinetic theory, in [58] the theory of absolute rates of chemical reactions is meant applied to connect the spreading velocity $v(t)$ with the dynamic contact angle θ [59]. Besides, an attempt was made to prove the relationship obtained in [11] (see also [14]) in terms of nonequilibrium thermodynamics:

$$v(t) = (\sigma / 9\eta)\left(\theta^2 - \theta_e^2\right)\ln\left(L/L_0\right) \qquad (7)$$

Here η is the dynamic viscosity of liquid, L is a characteristic length scale of the droplet, L_0 is the slip length. For this purpose in [58] the spreading Lennard-Jones droplets were simulated consisting of 25600 atom and located on a FCC-substrates with different values of the local substrate density d defined as the ratio of the substrate volume to the volume of the most close packed FCC. It is not quite clear why $d \le 1$ (0.5; 0.7; 0.75 and 1) as the close packed solid should have lower volume. The authors obtained dependence of θ on time t for different values of d and the linear dependence of $\cos\theta$ on d. However, the degree of justification of the Blake–Haynes half-empirical theory as well as of Eq. (7), containing the macroscopic value of the viscosity η, leaves many open questions.

First of all, it is not clear how the viscosity coefficient should be attributed to nanodroplets. Below we shall also make some estimations using formula (7). For nanodroplets L / L_0 is of order of 10. Respectively, $\ln\left(L / L_0\right) \sim 1$. Then, let use assume that $\theta = \pi / 2$ and $\theta_e = \theta / 2$. Finally, taking the values $\sigma = 10\,\text{mJ/m}^2$ and $\eta = 0.0282\,\text{Pa/s}$, corresponding to argon at $84.25\,\text{K}$, we obtain the value $v \sim 1$ m/s. This value seems to be adequate and corresponds to estimations obtained on the basis of our molecular dynamics result [21]. However, Eq. (7) was obtained for a macroscopic spreading droplet model. For such a model $L \sim 1$ mm and we shall obtain $v \sim 6$ m/s that is 1 to 2 orders higher than velocities observed for the most rapid, i.e. kinetic, regime of the macroscopic droplet spreading. So, Eq. (7) hardly can be applied for quantitative calculations even in the macroscopic case for which it was primary proposed, and it seems to be problematic to

87

justify this relationship using molecular dynamics results obtained for nanodroplets.

The second group of papers on the molecular dynamics of spreading has been conditionally referred to as the computer simulation of special cases of spreading. Let us begin with our paper [60] where the spreading droplets were simulated consisting of rod-like molecules. These molecules correspond to a limiting case of chain-like ones when the equilibrium valence angle $\alpha_e = 180^0$ and the chains in question are very ridged. The evolution of nanodroplets presented by rigid linear tetramers in the field of the high-energy substrate ($\varepsilon_s^* = 5$) resulted in a planar parquet structure of the first (lower) monolayer consisting of 2D-clusters with the parallel orientation of rod-like molecules (Fig. 3). Such a cluster may be interpreted as a domain with nematic ordering or as a 2D-crystallite. It seems to be principal that the rods in question consisted of separate interacting centers locating in the points of the 2D HCP lattice. The effect under discussion was discovered by my former post-graduate student V. V. Dronnikov. Likely to S. D. Muravyev, he was talented, capable and creative. His former supervisor P. V. Komarov recommended him as a genius of programming. We developed a very good program used up to the present time for simulation of Lennard-Jones nanoparticles in the force field of the solid surface.
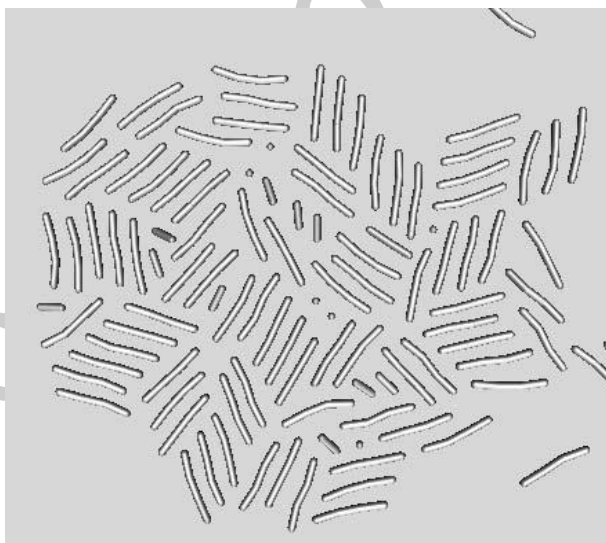

F i g . 3. The first (lower) monolayer formed after the spreading of a manodroplet consisting of rigid linear tetramers over the high-energy continual substrate with $\varepsilon_s = 5$

In [61] the spreading dynamics was investigated for nanodroplets of Lennard-Jones fluid and water on the basis of MD simulation. The authors emphasized that they studied the spreading on a wetting gradient. However, it

is not quite clear what they did mean under the wetting gradient. Such a notion is not used in the macroscopic theory of spreading. Besides, all the forces (inside the droplet and from the substrate) should be found in MD via an interatomic interaction potential and a potential of the substrate. Water is a complex enough system for computer simulation. So, a trial of a water system simulation is of special interest. In [61] the behavior of water droplets depending on the uniformity of the wetting gradient on substrates composed of methyl- and hydroxyl-terminated alkanethiol chains on Au (111) was also investigated. The most interesting is that, contrary to the Lennard-Jones droplets, water droplets 'walked' alone the substrate as a whole. It is explained by the non-uniformity of the wetting gradient. Presumably, the authors meant an anisotropic substrate. Otherwise, drifting droplets should be interpreted as an exhibition of the violation of the momentum conservation law.

In [62] MD was applied to study the influence of surfactants on the droplet spreading over solid surfaces. It is also noteworthy that in this paper, the situation was performed when the droplet in question is surrounded by a monatomic solvent. However, it is not clear why the solvent in question looks rather as the vapor in our snapshots and those in [44]. In other words, it seems that the surrounding liquid in [62] has the density several orders lower than the droplet density. In recent paper [63] the dynamics of droplet spreading was investigated by MD for the case of two immiscible fluids of equal density and viscosity. It is not clear how to satisfy the above condition for different liquids. Really, the fluid viscosity is defined by its density and parameters of the pair potential [33]. It is also of interest that for the liquid-liquid-solid triple line, the mentioned above diffusive law $R_1 \sim \sqrt{t}$ was also observed.

A very special type of spreading corresponds to the spreading of liquid metals over solid surfaces. In some cases, for example, at spreading of lead on copper, the substrate can be assumed to be chemically inactive [64]. The opposite situation corresponds to the so-called reactive wetting [65]. Being of interest, the paper [65] provokes, at the same time, some questions. Particularly, the authors mentioned a crossover from the inertial to diffusive spreading. The inertial regime is known in the theory of the macroscopic spreading, but it is not clear whether such a term can be applied to the nanodroplet spreading. From a general physical point of view, the inertia forces can be introduced into consideration in non-inertial reference systems only. Perhaps, in [65] the moving triple line is interpreted as such a reference system. However, for nanodroplets, the triple line, especially the moving edge, is not strictly differentiated as in the macroscopic case. Then, as was demonstrated in our paper [20], the motion of molecules in the triple line region is complex enough and corresponds, in general, to the rolling motion mechanism which seems to be not consistent with an inertia force acting

along the substrate. The nanodroplet spreading rates (of order of $1\,\text{m/s}$) are really higher than the rates of the bulk diffusion. However, preparing paper [21], we found some experimental data demonstrating that the surface diffusion rate can be much higher than the bulk one. So, the applicability of the inertial regime concept to nanosized droplets should be more thoroughly investigated in the future.

Molecular dynamics of nanodroplets on heterogeneous (structured) surfaces may be treated as another important direction of research. It is worth to mention that, contrary to some other authors, we believe that substrates with an atomistic (discrete) structure should not be referred to as heterogeneous. In [66] a special emphasis was made on the validity of the Cassie law

$$\sigma_{lv}\cos\theta_e = c(\sigma_{sv}^{(A)} - \sigma_{sl}^{(A)}) + (1-c)(\sigma_{sv}^{(B)} - \sigma_{sl}^{(B)}) \tag{8}$$

where superscripts A and B correspond to two different species on the substrate under consideration, c is the concentration of the species A. Unfortunately, it is not quit clear how a heterogeneous substrate was designed in this work, it is only mentioned that the substrate was constituted by one species A which interacts strongly with the droplet and species B, which interacts weakly. In paper [67] which was also prepared with participation of J. De Coninck, substrates were shown with quadratic inclusions. As a result, in [66, 67] a conclusion was made on the validity of the Cassie law 'for molecular heterogeneities'. Moreover, the authors of the paper showed that, provided the sizes of heterogeneities are of molecular scale, the geometry does not change the equilibrium contact angle θ_i.

In our papers [68, 69] we simulated the simple and polymer droplet spreading over heterogeneous surfaces of different types: (*i*) striped surfaces with adjacent high- and low-energy segments); (*ii*) high-energy surfaces with regular quadratic low-energy inclusions, (*iii*) low-energy surfaces with quadratic high-energy inclusions. It was found that the Cassie law was not always quantitatively satisfied. In this connection, we agree with the authors of [68, 69] that this law should be fulfilled when the sizes of inclusions are of molecular or mesoscopic scale (in the last case, relative to the molecule and droplet sizes). In the case of the striped surfaces, the droplet spreads along high-energy stripes whereas low-energy stripes play role of potential barriers preventing the spreading. As a result, the Cassie law will be violated. We should also note, that a proof of the Cassie law by means of a molecular dynamics research is not trivial problem. Really, in the general case, the macroscopic surface tensions σ_{lv}, σ_{sv} and σ_{se} hardly can be adequately attributed to computer models in question. So, only under some special conditions [68], the results of computer experiments can be compared with those predicted by the Cassie law. There are also some other 'technical'

problems concerning computer simulation of spreading on heterogeneous surfaces. Particularly, it is not easy to take into account forces acting on a droplet molecule (or an interacting center) along the substrate at the species boundaries. In [68] we introduced into consideration a small but finite in width transitional region between the segments with different values of ε_s^*. In this way it becomes possible to find the lateral force via the gradient of the substrate potential. It is also remarkable that in the case of quadratic low-energy inclusions (2×2 in molecular diameters), the diffusive law $R_1 \sim \sqrt{t}$ is also fulfilled. Therefore the value $n = 1/2$ of the exponent n in the exponential dependence (1) seems to be a magic number which corresponds exactly or roughly to the available results of laboratory and computer experiments on nanodroplets spreading.

In [70] an accurate molecular dynamics research of the nanodroplet spreading over striped surfaces (they are referred to as 'chemically patterned surfaces') was performed. The results are presented for polymer droplets on substrates consisting of alternating stripes characterizing by the equilibrium contact angles $\theta_i = 0°$ and $\theta_i = 90°$. The droplet spreading was compared for patterns of different wavelength and strength of surface interaction of the wetting stripes. For small wavelengths droplets partially spread on both the wetted and non-wetted regions of the substrate.

5. Conclusion. In this review we have analyzed publications on computer simulation of the droplet spreading for the last 20 years, i.e. during the whole history of the research in this field of surface science (first papers of 1971 by E. D. Shchukin and V. S. Yushchenko are considered as precursors of this scientific direction). A special emphasis was made on the papers of last years. An evaluation of advances and problems in this field of research should be obviously based on a concept reflecting main goals of the computer simulation of spreading. Our own concept is that the goals of these investigations may be divided into fundamental and applied ones. From the fundamental point of view, two goals may be formulated: (*i*) to elucidate laws and mechanisms of the macroscopic spreading; (*ii*) to discover specific features of the nanodroplet spreading. The applied goal is to predict some new technical decisions and new technologies at macroscopic and nanoscale levels involving the wetting and spreading processes. For example, the spreading on structured surfaces can be used to produce new nanocomposite materials.

As for fundamental aspect of the droplet spreading simulation, some advances really can be highlighted. Particularly, it has been finally found that in general the nanodroplet spreading kinetics follows the law $R_1 \sim \sqrt{t}$ though deviations from this law are also numerous and, respectively, this dependence should be rather treated as a tendency than the law. Besides, it is now clear that this law really corresponds to the surface diffusion of molecules along

the substrate. It is also worth to mention that computer simulation confirmed in general the mentioned above opinion of P. de Gennes that the simple (non-polymer) liquid spreading corresponds to the rolling motion mechanism, whereas polymer liquid spreads because of the special type of the chain slippage. The fact that the authors of the last papers on spreading simulations have tried to compare their results with the former theories of macroscopic spreading also should be evaluated positively.

However, some problems in this field should be also discussed. We have seen that in many cases the authors do not clearly distinguish the results which should be attributed to nanosystems only and the results which seem to have a more general field of the applicability, i.e. are valid for the nanoscale and macroscopic spreading. Particularly, macroscopic quantities, like the surface and interfacial tensions, and theoretical results, obtained for macroscopic droplet models, are used at the nanoscale level without proper analysis and corrections. In the previous section we also noted that the macroscopic notion of the viscosity is also used in publications on computer simulation of spreading without any justification of the correctness of macroscopic approaches compared with the computer experiments for nanodroplets.

All the above reviewed papers on special cases of spreading are, of course, of interest from the applied point of view, because just the computer simulation, especially using supercomputers seems to be able to predict the spreading and wetting behavior on different types of substrates, including structured ones. However, so far there are no noticeable results in utilizing the computer simulations of spreading for the development or improvement of modern macro- or nanotechnologies. In particular, among the problems still waiting for their solution is the problem of production of non-wettable surfaces.

References

1. Hocking L.M. A moving fluid interface on a rough surface // J. Fluid Mech. 1976. V. 76. P. 801–817.
2. Ruckenstein E., Dunn C.S. Slip velocity during wetting of solids // J. Colloid Interface Sci. 1977. V. 59. P. 135138.
3. Neogi P., Miller C.A. Spreading kinetics of a drop on a smooth solid surface // J. Colloid Interface Sci. 1982. V. 86. P. 525–538.
4. Dussan E.B. The moving contact line: the slip boundary conditions // J. Fluid Mech. 1976. V. 77. P. 665–684.
5. Hocking L.M. A moving fluid interface. Part 2. The removal of the force singularity by a slip flow // J. Fluid Mech. 1976. V. 79. P. 209–229.
6. Hocking L.M. Sliding and spreading of thin two-dimentional drops // Q. J. Meca. Applied Math. 1981. V. 34. P. 37–55.
7. Hocking L.M., Rivers A.D. The spreading of a drop by capillary action // J. Fluid Mech. 1982. V. 121. P. 425–442.
8. Lacey A.A. The Motion with slip of a thin viscous droplet over a solid surface. Studies in Applied Math. 1982. V. 67. P. 217–230
9. Starov V.M. On spreading of droplets of nonvolatile liquids over flat solid surface // Kolloidn Zhurn. 1983. V. 45. P. 1154 – 1161 (in Russian).
10. Starov V.M, Velarde M.G and Radke C.J. Wetting and spreading dynamics, CRC Press, Taylor & Francis Group, 2007.
11. de Gennes P.G. Physique des surfaces et des interfaces.–Dynamics detalement d'une goutte // C. R. Acad. Sc. Paris Serie II. 1984. V. 298. P. 111–115.
12. Samsonov V.M, Shcherbakov L.M. The nonequilibrium thermodynamics of the wetting perimeter. The thermodynamics characteristics of the wetting perimeter. The equation of balance // Kolloidn. Zhurn. 1985. V. 47. P. 729–736.
13. Summ B.D, Samsonov V.M. Concepts of Rehbinder's school and modern theories of spreading // Colloids and Surfaces. A. 1999. V. 160. P. 63–77.
14. de Gennes P.G. Wetting statistics and dynamics // Rev. Mod. Phys. 1985. V. 57. P. 828–863.
15. Hardy W.B. Collected Works, Cambridge. 1936.
16. Benny D.J, Timson W.J. The rolling motion of a viscous fluid on and off a rigid surface // Studies in Applied Mathematics. 1980. V. 63. P. 93–98.
17. Dussan E.B, Davis S.H. On the motion of a fluid-fluid interface // J. Fluid Mech. 1974. V. 65. P. 71–95.
18. Dussan E.B. On the spreading of liquids on solid surfaces: static and dynamic sontact lines // Ann. Rev. Fluid Mech. 1979. V. 11. P. 371–400.
19. Churaev N.V, Sobolev V.D, Somov A.N. Slipping of liquids over lyophobic solid surfaces // J Colloid Interface Sci. 1984. V. 97. P. 574–581.
20. Samsonov V.M, Ratnikov A.S. Comparative molecular dynamics study of simple and polymer nanodroplet spreading // Colloids and Surfaces A. 2007. V. 298. P. 52–57.
21. Samsonov V.M, Zhukova N.A, Dronnikov V.V. Molecular-dynamic simulation of nanosized droplet spreading over continual solid surface // Colloid J. 2009. V. 71. P. 835–845.
22. Miller C.A, Puckenstein E. The Origin of Flow during Wetting of Solids // J. Colloid Interface Sci. 1974. V. 48. P. 368–373.

23. Leger L., Joanny J.F. Liquid spreading // Rep. Prog. Phys. 1992. V. 55. P. 431–485.
24. Bonn D., Eggers J., Indekeu J., Meunier J. and Rolley E. Wetting and spreading // Rev. Mod. Phys. 2009. V. 81. P. 739–805.
25. Marmur A. Equilibrium and spreading of liquids on solid surfaces // Colloid Interface Sci. 1983. V. P. 75–105.
26. Lelah M.D, Marmur A. Spreading kinetics of drops on glass // J. Colloid Interface Sci. 1981. V. 82. P. 518–525.
27. Tanner L.H. The spreading of silicon oil drops on horizontal surface // J. Phys. D. 1979. V. 12. P. 1473–1484.
28. Soboleva O.A. et al. Crossover from the inertial to viscous regime of spreading // Kolloidn. Zhurn. 1989. V. 51. P. 1204–1207 (in Russian).
29. Kwei T.K. et. al. Kinetics of wetting of surfaces by polymer melts // Colloid Interface Sci. 1968. V. 28. P. 543–546.
30. Samsonov V.M. On the similarity in the kinetics of spreading of small droplets on solid surfaces // Colloid J. 1997. V. 59. P. 482–487.
31. Marx D. Hutter J. Ab initio molecular dynamics: theory and implementations. Modern methods and algorithms of quantum chemistry / J Grotendorst Ed. Julich. John von Neumann Institute for Computing 2000. 301–349.
32. Allen M.P, Tildesley D.J. Computer simulation of liquids. Oxford: Clarendon press. 1990.
33. Croxton C. Liquid state physics. Cambridge: C. University press. 1974.
34. Niemunen J.A., Abraham D.B., Kattunen M., Kashi K. Molecular dynamics of a microscopic droplet on solid surface // Phys. Rev. Lett. 1992. V. 69. P. 124–127.
35. Shchukin E.D, Yushchenko V.S. Molecular dynamics of wetting // Kolloidn. Zhurn. 1977. V. 39. P. 331–334 (in Russian).
36. Yushchenko V.S., Jrivtsov A.F., Shchukin E.D. Stability and dynamics of droplet on the surface of a solid body // Kolloidn. Zhurn. 1977. V. 39. P. 335–338 (in Russian).
37. Summ B.D., Yushchenko V.S., Shchukin E.D. Hydrodynamics and physicochemical aspects of spreading // Colloids and Surfaces. 1987. V. 27. P. 43–55.
38. Heslot F, Fraysse N, Cazabat A.M. Molecular layering in the spreading of wetting liquid drops // Nature. 1989. V. 338. P. 640–647.
39. De Coninck J., Fraysse N., Valignat M.P., Cazabat A.M. A microscopic simulation of the spreading of layered droplets // Langmuir. 1993. V. 9. P. 1906–1909.
40. Samsonov V.M., Muravyev S.D., Khalatur P.G. Monte-Carlo Simulation of the Spreading Process of Nanosized Liquid Droplets on Solid Surface // Colloid J. 1998. V. 60. P. 367–373.
41. Samsonov V.M., Muravyev S.D., Kirillova M.A. Numerical Modeling of the Kinetics of Spreading of Nanometer-scale Drops of Simple and Polymer Liquids // Russian J. Phys. Chem. 1998. V. 72. P. 599–605.
42. Samsonov V.M., Muravyev S.D. Molecular dynamics modeling of the evolution of nanosized polymer particles in the field of solid surface // Rus. J. Phys. Chem. 2000. V. 74. P. 1796–1803.
43. Fox H., Zisman W. The Spreading of Liquids on Low Energy Substrates. I. Polytetrafluoroethylene // J. Colloid Sci. 1950. V. 5. P. 514–531.

44. Heine D.R., Grest G.S., Webb III E.B. Spreading dynamics of polymer nanodroplets // Phys. Rev. E. 2003. V. 68. P. 61603–61603.
45. Yang J., Koplik J. and Banavar J.R. Molecular dynamics of drop spreading on a solid surface // Phys. Rev. Lett. 1991. V. 67. P. 3539–3542.
46. Nieminen J.A., Abraham D.B., Karttunen M., Kaski K. Molecular dynamics of a microscopic droplet on solid surface // Phys. Rev. Lett. 1992. V. 69. P. 124–127.
47. Nieminen J.A., Ala–Nissila T. Dynamics of Spreading of Small Droplets of Chainlike Molecules on Surfaces // Europhysics Lett. 1994. V. 25. P. 593–598.
48. de Coninck J., D'Ortona U., Koplik J., Banavar J.R. Terraced Spreading of Chain Molecules via Molecular Dynamics // Phys. Rev. Lett. 1995. V. 74. P. 928–931.
49. Wagner L. Molecular Dynamics Simulation of Polymer Droplets // Phys. Rev. E. 1995. V. 51. P. 499–503.
50. Blake T.D., Clarke A., De Coninck J., Ruijter M.J. Contact angle relaxation during droplet spreading: comparison between molecular kinetic theory and molecular dynamics // Langmuir. 1997. V. 13. P. 214–2166.
51. De Gennes P.G. Scaling Concepts in Polymer Physics, Cornell University Press. Ithaca, 1979.
52. Heine D.R., Grest G.S., Webb III E.B. Spreading dynamics of polymer nanodroplets in cylindrical geometries // Phys. Rev. E. 2004. V. 70. P. 11606.
53. Voue M., Rovillard S., De Coninck J. Spreading of liquid mixtures at the microscopic scale: a molecular dynamics study of the surface-induced segregation process // Langmuir. 2000. V. 16. P. 1428–1435.
54. Seveno D., Ledauqhin V., Martic G., Voue M., De Coninck J. Spreading drop dynamics on porous surfaces // Langmuir. 2002. V. 18. P. 7496–7502.
55. Bertrand E., Blake T.D., De Coninck J. Spreading dynamics of chain-like monolayers: a molecular dynamics study // Langmuir. 2005. V. 21. P. 6628–6635.
56. Benhassine M., Saiz E., Tomsia A.P., De Coninck J. Nonreactive spreading at high-temperature revisited for metal systems via molecular dynamics // Langmuir. 2009. V. 25. P. 11450–11458.
57. Bertrand E., Blake T.D., De Coninck J. Influence of solid-liquid interactions on dynamic wetting: a molecular dynamics study // J. Phys.: Condens. Matter. 2009. V. 21. P. 464124–464137.
58. Seveno D., Dunter N., De Coninck J. Wetting dynamics of drop spreading. New evidence for the microscopic validity of the molecular-kinetic theory // Langmuir. 2010. V. 26. P. 14642–14647.
59. Blake T.D., Haynes J.M., Contact angles hysteresis,– Progress in surface and membrane. London–N.Y.: Acad. Press 1973. V. 6. P. 125–138.
60. Samsonov V.M., Dronnikov V.V. Molecular dynamics study of structure formation at spreading of nanodroplets composed of rod-like molecules. Colloids and Surfaces. 2004. V. 239. P. 119–124.
61. Halverson J.D., Maldarelli C., Couzis A., Koplink J. A molecular dynamics study of the motion of a nanodroplets of pure liquid on a wetting gradient // J. Chem. Phys. 2008. V. 129. P. 164708–1–164708–12.
62. Shen Y., Couzis A., Koplik J., Maldarelli C., Tomassone M.S. Molecular dynamics study of the influence of surfactant structure on surfactant–facilitated

spreading of droplets on solid surfaces // Langmuir. 2005. V. 21. P. 12160–12170.

63. Wu C., Qian T., Ping Sheng Droplet spreading driven by van der Waals force: a molecular dynamics study // J. Phys.: Condens. Matter. 2010. V. 22. P. 325101–325102.

64. Webb III E.B., Grest G.S., Heine D.R. Precursor film comtrolled wetting of Pb on Cu // Phys. Rev. Lett. 2003. V. 91. P. 236102–1–236102–4.

65. Wheeler D., Warren J.A., Boettinger W.J. Modeling the early stages of reactive wetting // Phys. Rev. E. 2010. V. 82. P. 051601–1–051601–14.

66. Adao M.H., De Ruijter M., Voue M., De Coninck J. Droplet spreading on heterogeneous substrates using molecular dynamics // Phys Rev. E. 1999. V. 59. P. 746–749.

67. Voue M., Semal S., De Coninck J. Dynamics of spreading on heterogeneous substrates in a complete wetting regime // Langmuir. 1999. V. 15. P. 7855–7862.

68. Samsonov V.M., Dronnikov V.V., Volnukhina A.A., Muravyev S.D. Molecular dynamical simulation of structure formation after nanodroplet spreading over heterogeneous surfaces // Surf. Sci. 2003. V. 532. P. 560–566.

69. Samsonov V.M., Dronnikov V.V., Pushkar M.Yu., Nikiforova E.V., Filippov A.I., Muravyev S.D. Molecular dynamics study of nanoscale structure formation in droplet spreading on solid surfaces // J. Material Sci. 2005. V. 40. P. 2389–2394.

70. Grest G.S., Heine D.R., Webb III E.B. Liquid nanodroplets spreading on comically patterned surfaces // Langmuir 2006. V. 22. P. 4745–4749.

TWENTY YEARS OF COMPUTER SIMULATION OF DROPLET SPREADING

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Обзор посвящён двадцатилетию с начала публикаций работ по компьютерному моделированию процессов растекания капель. Выделены работы автора данного обзора и его коллег. После краткого обзора основных результатов по макрорастеканию и характеристики методов компьютерного моделирования даётся критический обзор исследований в данной области. Как следует из обзора, начало исследований в этой области науки о поверхностных явлениях относится к 1990 г.

Ключевые слова: растекание капель, смачивание, компьютерное моделирование, критический обзор

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