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Molecular dynamics study of nanoscale structure formation in droplet spreading on solid surfaces

V. M. SAMSONOV*, V. V. DRONNIKOV, M. YU. PUSHKAR, E. V. NIKIFOROVA, A. I. FILIPPOV, S. D. MURAVYEV
Tver State University, Brigadnaya, 37, Tver 170027, Russia
E-mail: Vladimir.Samsonov@tversu.ru

Spreading of nanosized droplets was simulated on the basis of the isothermal molecular dynamics. A conclusion is made that the nanoscale droplet evolution has many common features with the macroscopic spreading. At the same time, some structure formation processes are revealed specific for the nanosized region. Observed effects include: the pyramid-like structure formation, the orientational ordering and the parquet cluster structure formation in nanodroplets composed of rod-like molecules, the replication of the structured (heterogeneous) surfaces represented by high- and low-energy segments such as striped substrates and surfaces with quadratic high- and low-energy inclusions.

1. Introduction

Spreading phenomena are related to many fundamental and applied problems important for numerous natural and technological processes, e.g. surface covering, adhesion, spray painting, welding and soldering [1–2]. Obviously, some macroscopic technological processes, e.g. soldering and producing composite materials, may be extended to nanoscale systems. At the same time, structure formation processes are expected specific for the nanosized region. Up to the present, the design of nanostructures on solid interfaces is based on the next methods: (i) with the aid of a precise instrument, such as the tip of an atomic force microscope; (ii) by directed chemical synthesis; (iii) providing conditions for the self-organization of nanostructures located in the force field of the solid surface.

The term ‘self-organization’ was first used in non-equilibrium thermodynamics [3] being attributed to so-called dissipative (Bertalanffy’s) structures arising far from the thermodynamic equilibrium under some additional necessary conditions. However, during last decades, this term has been widely used, particularly by Lehn [4], for the self-assembly of any less or more regular ordered structures which, as a rule, do not correspond to Bertalanffy’s definition. Such a modern meaning of the term under consideration is assumed in this paper. Among others, the term ‘self-organization’ is used in [5] for the Ge-pyramid formed by germanium atoms on the silicon substrate [6–17]. Such structures produced by the epitaxial growth (Stranski-Krastanow processes) can be, particularly, used as quantum dots. In this paper the hypothesis is advanced and justified that pyramid-like structures can be obtained not only by the Stranski-Krastanow processes but also using the nanodroplet spreading concurrent with the crystallization.

In accordance with the results of our previous works [18–19], the spreading of Lennard-Jones nanodroplets reproduces many principal features of the spreading and self-organization processes in high-temperature systems, i.e., in metallic nanodroplets. The results of these works demonstrate that the covalent nature of the interatomic interactions is not necessary for the pyramid-like structure formation. Really, the structures of this type have been observed in our molecular dynamical experiments on Lennard-Jones systems.

As noted by Lehn [4], the more complex are molecules, the more possibilities should be for self-organization processes. We have observed some effects of the self-organization, namely the liquid crystal ordering and the cluster (domain) structuring, in systems composed of complex molecules, particularly of rigid rod-like molecules.

One of the most important designable factors of the self-organization in the nanodroplet spreading is the structure of the solid substrates [20]. Macroscopic spreading over substrates of this type was experimentally studied by Y. Naidich *et al.* [21]. We have studied the nanodroplet spreading over structured (heterogeneous) surfaces with mesoscopic heterogeneities (striped surfaces, surfaces with quadratic mesoscopic high- and low-energy inclusions). The term ‘mesoscopic’ is used as it was introduced into consideration in synergetics [22]. According to [22], the linear scale of the macroscopic level corresponds to the size of the whole system under consideration; the microscopic

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*Author to whom all correspondence should be addressed.

level refers to separate atoms or molecules; whereas the intermediate, i.e., mesoscopic, level is attributed to the structures with characteristic linear parameters greater than the atomic size but smaller than the system dimension. One of the goals of this work is to elucidate some objective laws of the spreading which are general for both: macroscopic and nanoscale systems. In particular, it has been found that as a rule the macroscopic Cassie law [23], which may be treated as an extension of the Young equation on heterogeneous surfaces, is also valid at the nanoscale size region.

2. Method of simulation

In our previous papers [18, 19, 24–26], the spreading of Lennard-Jones droplets was simulated using both molecular dynamics and Monte Carlo. The metallic droplet spreading was also simulated on the basis of the Monte Carlo method. The results obtained for metallic systems using specific effective pair potentials agree, in general, with the results for Lennard-Jones droplets if the parameters of the Lennard-Jones potential are chosen to be adequate to corresponding metal melts. In this work we have used our program for the isothermal molecular dynamics simulation of the evolution of Lennard-Jones nanoparticles in the force field of the solid substrate by invoking the Berendsen thermostat [27]. The shape of the starting drop corresponds to a sphere of initial radius R_0 with its centre located at the distance $R_0 + a_\mathrm{l}$ from the smooth solid surface where a_l is the effective atomic diameter.

Assuming that the interaction between two molecules in the liquid-vapor subsystem and in the solid, correspondingly, is characterized by the Lennard-Jones pair potential

$$\Phi(r) = 4\varepsilon_\mathrm{sl}\left[\left(\frac{a_\mathrm{sl}}{r}\right)^{12} - \left(\frac{a_\mathrm{sl}}{r}\right)^{6}\right], \qquad (1)$$

and integrating over the solid half-space, we can readily obtain the next expression for the reduced potential of the solid substrate

$$u^*(z^*) = \frac{u(z)}{4\,\varepsilon_\mathrm{l}} = \frac{D}{z^{*9}} - \frac{C}{z^{*3}}. \qquad (2)$$

In (1) r is the interatomic distance, ε and a are the energetic and the linear parameters of the pair potential, respectively. It is convenient to express ε_sl and a_sl (subscripts s and l correspond to the solid substrate and the droplet-vapor subsystem respectively) in terms of the corresponding parameters of the interaction in the liquid-vapor (ε_l, a_l) and solid (ε_s, a_s) subsystems [28]: $\varepsilon_\mathrm{sl} = \sqrt{\varepsilon_\mathrm{s}\varepsilon_\mathrm{l}}$, $a_\mathrm{sl} = (a_\mathrm{s} + a_\mathrm{l})/2$, where a_s and a_l can be interpreted as the effective atomic diameters in the solid and the liquid-vapor subsystem, respectively. Then, $z^* = z/a_\mathrm{l}$ is the reduced coordinate (the z-axis is normal to the solid interface), C and D are the attraction and repulsion constants, respectively. Particularly, $C = \pi n_\mathrm{s} a_\mathrm{s}^3 \left(\varepsilon_\mathrm{s}/\varepsilon_\mathrm{l}\right)^{1/2}/6$ [24]. Varying the ratio $\varepsilon_\mathrm{s}/\varepsilon_\mathrm{l} = \varepsilon_\mathrm{s}^*$, we can reproduce cases of low-energy ($\varepsilon_\mathrm{s}^* = 0.5-2$) and high-energy ($\varepsilon_\mathrm{s}^* = 5-50$) substrates [24].

The molecular dynamics and Monte Carlo evolution do not depend on the absolute temperature itself but on the reduced temperature $T^* = kT/\varepsilon_\mathrm{l}$ (k is the Boltzmann constant). The value $T_\mathrm{m}^* = 0.65$ corresponds to the macroscopic melting temperature of such non-polar liquids as noble gases and benzene.

3. Molecular dynamic simulation of pyramid-like structure formation in concurrent nanodroplet spreading and crystallization

As was mentioned above, germanium islands formed during Ge/Si heteroepitaxy have been the subject of intense studies during the last decade [6–17]. Thus, a great effort has been devoted to unravel the island nucleation process, and to elucidate the crucial factors that drive this effect. In [8], a crucial role in the Ge-pyramid formation is ascribed to a mismatch of their lattices: Ge has 4% larger lattice constant than Si. As a result, high stresses and strains arise in the Ge/Si islands [13] mediating the pyramid-like nanocrystal formation.

However, despite this progress, the nature of the pyramid-like structure formation is not quite clear. Particularly, it is worth to investigate whether the covalent nature of the interatomic interaction in Ge/Si systems is necessary for the pyramid-like structure formation. It is also of interest whether pyramid-like structures can be obtained by other ways different from the Stranski-Krastanow processes [29]. In this paper, the next working hypotheses is put forward: (i) the pyramid-like structure formation is not specific for the Ge/Si system; (ii) there exists a basic relationship between the pyramid-like structure formation and the wetting behavior of corresponding nanodroplets on the same solid substrate; (iii) pyramid-like structures can be obtained not only by the vapor (atomic beam) deposition but also in the nanodroplet spreading.

There exists an interesting correlation between the pyramid-like structure formation and the wetting of crystal faces by own melt droplets. This correlation is caused by very close values of effective linear a and energetic ε parameters for germanium and silicon. It should result in a similar wetting behavior of Ge(l)/Si(s) and Ge(l)/Ge(s) systems as well as of the Lennard-Jones system with the same values of a and ε parameters. Really, the wetting of poly- and single crystals by the own melt, including systems Ge(l)/Ge(s) and benzene(i)-benzene(s) is characterized by small enough but finite values 20–30° of the equilibrium contact angle θ_e [30]. These experimental data on the wetting agree with the angle 18° between the side and the base of the Ge-pyramid described in [5]. This pyramid is about 1.5 nm high and 10 nm in its quadratic base. Respectively it consists of about 3000 atoms of germanium.

The final (quasistatic) configuration of a Lennard-Jones nanodroplet containing 3000 atoms after the spreading over the Lennard-Jones solid substrate with the parameters $a_\mathrm{s}^* = a_\mathrm{s}/a_\mathrm{l} = 0.95$, $\varepsilon_\mathrm{s}^* = \varepsilon_\mathrm{s}/\varepsilon_\mathrm{l} = 1.125$ (corresponding to the parameters

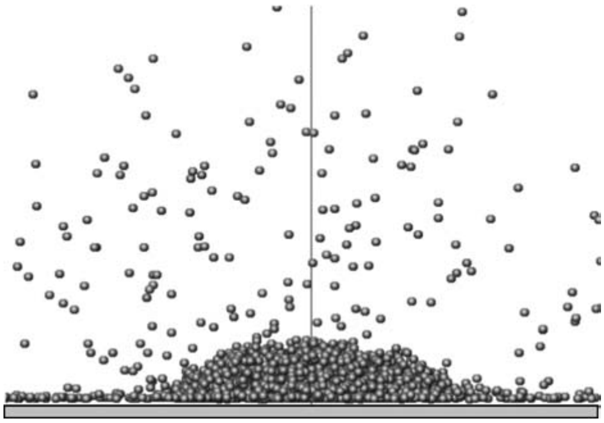

Figure 1 The final configuration after the wetting of the Lennard-Jones substrate by an own melt nanodroplet ($a_{\mathrm{s}}^* = \varepsilon_{\mathrm{s}}^* = 1$, $T^* = 0.65$).

of the Ge(l)/Si(s) system) is shown in Fig. 1 ($T^* = 0.65$). For the case in question, $a_{\mathrm{s}}^* \approx 1$ and $\varepsilon_{\mathrm{s}}^* \approx 1$. So, the droplet evolution and the final state of the above system practically coincides with these in the case of the wetting of the solid surface by the own melt droplet. The droplet presented in Fig. 1 forms the equilibrium contact angle 20–30°. However, this configuration does not have a regular pyramid-like structures. Then, if the droplet evolutes under the gradually cooling, i.e., under diminishing temperature from $T^* = 0.65$ to $T^* = 0.16$, the concurrent spreading and crystallization processes result in layered, pyramid-like structure formation. One of the final molecular dynamics configurations is shown in Fig. 2. In accordance with the "snapshot" of the germanium pyramid presented in [5] and reconstructed after the AFM image, the silicon substrate has some grooves which probably correspond to the grain boundaries. In our molecular dynamical experiments, these grooves were reproduced by narrow high-energy stripes (energetic wells) which form a regular netted structure on the substrate. It has been found that such a net of a very small relative area promotes the regular pyramid-like structure formation. As it could be expected, there are some principal distinctions of Lennard-Jones pyramids from germanium ones. Particularly, our pyramids have the crystalline structure with the first coordination number $N_1 \approx 12$. This value of the coordination number could correspond to fcc and hcp-structures. We have found that the hcp-structure is formed in Lennard-Jones pyramids obtained in our computer experiments. As a result, the base of Lennard-Jones pyramids is rather hexagonal that quadratic.

4. Structure formation in the spreading of nanodroplets composed of rod-like molecules

As was mentioned above, some other self-organization processes should appear in systems composed of complex (polyatomic) molecules. The case of rigid rod-like molecules has been proved to be the most interesting. The evolution of nanodroplets presented by rigid linear tetramers i.e., by rods consisting of four interacting centers, in the field of the high-energy substrate $\left(\varepsilon_{\mathrm{s}}^* = 5\right)$ results in a planar parquet structure of the first (lower) monolayer consisting of 2D-clusters with the parallel orientation of rods (Fig. 3). Such a cluster may be interpreted as a domain with the nematic ordering [31] or as a 2D-crystallite in dependence on the value of the order parameter. It is also noteworthy that the interacting centers of the linear molecules under discussion locate in the points of the 2D hcp lattice. In detail, the results of our molecular dynamics study of structure formation at spreading of nanodroplets composed of rod-like molecules are presented in [32].

5. Structure formation in the nanodroplet spreading over heterogeneous surfaces

We simulated the spreading of nanosized Lennard-Jones droplets over heterogeneous surfaces represented by high and low-energy segments: (1) the striped surface formed by segments with $\varepsilon_{\mathrm{sA}}^* = \varepsilon_{\mathrm{sA}}/\varepsilon_{\mathrm{l}} = 0.5$ and $\varepsilon_{\mathrm{sB}}^* = 5$; (2) the low-energy substrate ($\varepsilon_{\mathrm{sA}}^* = 0.5$) with quadratic high-energy inclusions ($\varepsilon_{\mathrm{s}}^* = 5$); (3) the high-energy substrate ($\varepsilon_{\mathrm{sB}}^* = 5$) with quadratic low-energy inclusions ($\varepsilon_{\mathrm{sA}}^* = 0.5$). Macroscopic analogs of the cases 1 and 2 were investigated in laboratory experiments by Naidich *et al.* [21].

In the case of quadratic high-energy inclusions ($c_{\mathrm{B}} = 1/4$) on the low-energy substrate ($c_{\mathrm{A}} = 3/4$), the incomplete wetting with the contact angle of the order

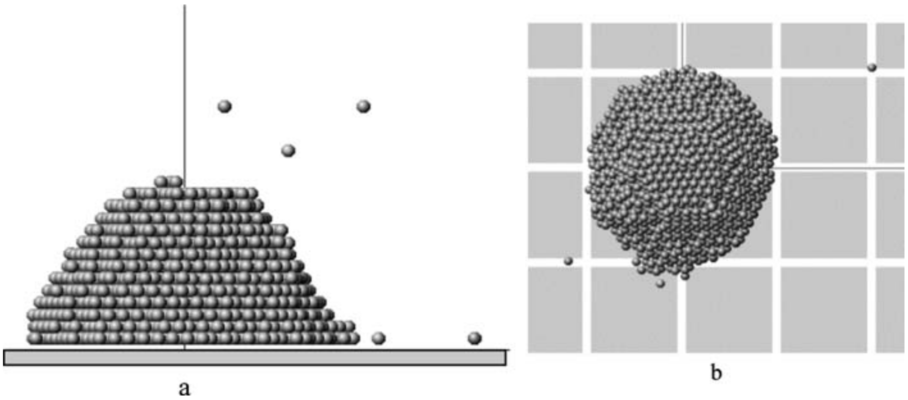

Figure 2 A snapshot of a pyramid-like structure formed after the concurrent spreading and crystallization process: a–a lateral sight; b–the sight from the above. White stripes on the substrate correspond to high-energy segments and reproduce the grain boundaries.

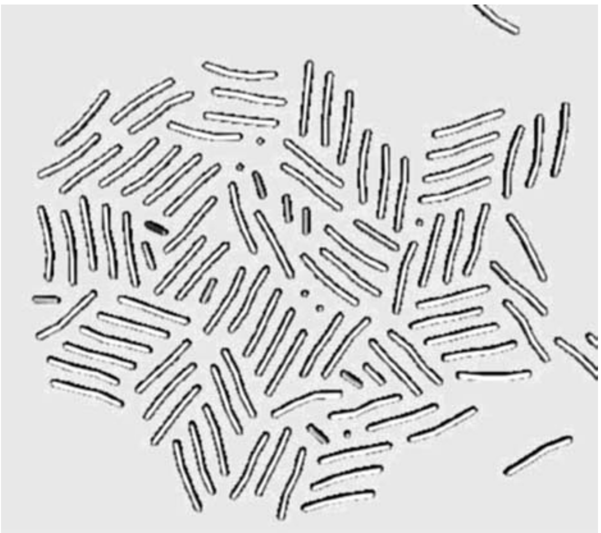

Figure 3 The first (lower) monolayer formed after the spreading of a nanodroplet consisting of rigid linear tetramers over the high-energy continuous substrate with $\varepsilon_s^* = 5$.

of 30° was observed (Fig. 4). In the case of quadratic low-energy inclusions ($c_A = 1/4$), the complete wetting was found, i.e., the formation of an island monolayer (Fig. 5).

In view of the 200th anniversary of the classical Young equation

$$\cos\theta_e = \frac{\gamma_{sv} - \gamma_{se}}{\gamma_{ev}}, \tag{3}$$

it is worth to discuss the validity, on the nanoscale level, of Equation (3) and the Cassie law [23]

$$\gamma_{lv}\cos\theta_e = c\left(\gamma_{sv}^{(A)} - \gamma_{sl}^{(A)}\right) + (1-c)\left(\gamma_{sv}^{(B)} - \gamma_{sl}^{(B)}\right) \tag{4}$$

which may be treated as an extension of Equation (3) to the heterogeneous surfaces. On one hand, the validity of the Young Equation (3), at least on a qualitative level, follows from the above mentioned agreement with the macroscopic equilibrium contact angle $\theta_e$in the case of the wetting of the solid surface by the own melt. On the other hand, a correct enough determination of the values of surface tensions $\gamma_{\alpha\beta}$ $(\alpha, \beta = s, l, v)$ for nanoscale systems seem to be impossible. However, concentrations (relative areas) c_A and c_B of species A and B can be determined quite correctly. So, the validity of the Cassie law (4) for surfaces with mesoscopic (nanoscale) heterogeneities may be investigated

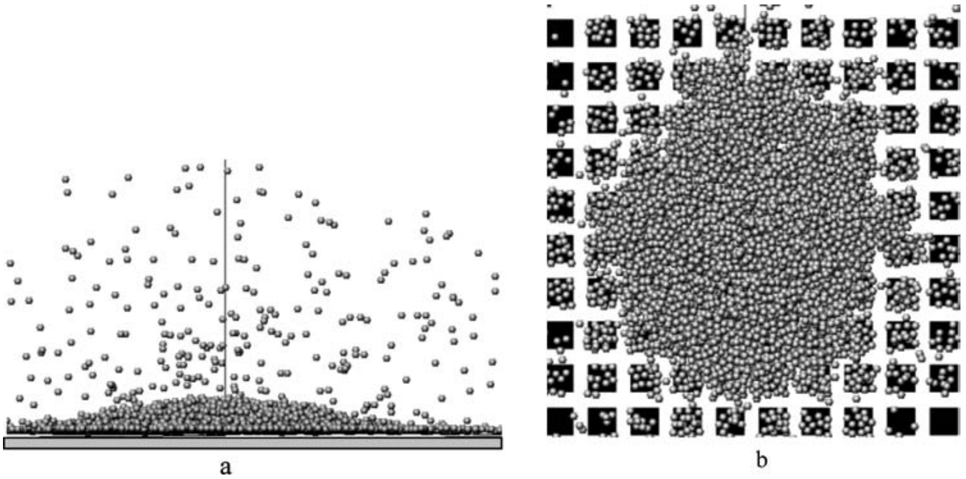

Figure 4 The final nanodroplet configuration after the spreading over the low-energy substrate ($\varepsilon_{sA}^* = 0, 5 \quad c_A = 3/4$) with regularly deposed quadratic (2 × 2) high-energy inclusions ($\varepsilon_{sB}^* = 0, 5 \quad c_B = 1/4$): a—a lateral snapshot, b—the site from the above.

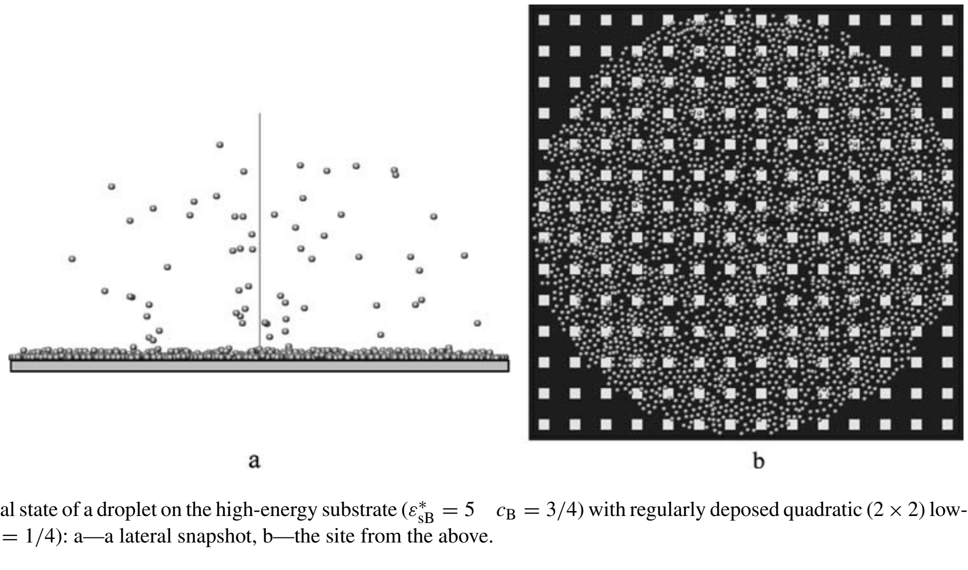

Figure 5 The final state of a droplet on the high-energy substrate ($\varepsilon_{sB}^* = 5 \quad c_B = 3/4$) with regularly deposed quadratic (2 × 2) low-energy inclusions ($\varepsilon_{sA}^* = 0, 5 \quad c_A = 1/4$): a—a lateral snapshot, b—the site from the above.

in comparative laboratory or computer experiments on different systems which, however, are characterized by the same values of the parameters $\gamma^{(\mathrm{i})}_{\alpha\beta}(i = A, B)$. The results of our previous molecular dynamics experiments on this topic were presented in [19]. A more accurate study of the problem under discussion is presented in this work.

In our molecular dynamics experiments, the chosen low-energy substrate with the parameters $\varepsilon^*_{\mathrm{sA}} = 0.5$ and $c_{\mathrm{A}} = 3/4$ had quadratic high-energy inclusions characterized by $\varepsilon^*_{\mathrm{SB}} = 5$ and $c_{\mathrm{B}} = 1/4$. In this case, the equilibrium contact angle $\theta_{\mathrm{e}} \approx 30^\circ$ was observed (Fig. 4). The same value of θ_{e} was observed when $\varepsilon^*_{\mathrm{sA}} = 0.5$, $c_{\mathrm{A}} = 3/4$ corresponded to inclusions and, respectively, $\varepsilon^*_{\mathrm{sB}} = 5$, $c_{\mathrm{B}} = 1/4$ to the basic substrate. So, for the above two systems with much lower concentration c_{B} of the high-energy component, the Cassie law (4) is fulfilled.

However, when $c_{\mathrm{A}} = 1/4$, which corresponds to low-energy inclusions, the complete wetting was observed. At the same time if the low-energy component with $c_{\mathrm{A}} = 1/4$ is presented by the basic surface covered by quadratic high-energy inclusions, a small but finite equilibrium contact angle $\theta_{\mathrm{e}} = 15^\circ$ was found. So, for the last two systems ($c_{\mathrm{A}} \ll c_{\mathrm{B}}$), the Cassie law (4) is satisfied only qualitatively.

6. Discussion

Up to the present, there are a number of papers on simulation of the Ge-pyramid [11, 13, 14] using the Tersoff potential [33], i.e., a many body potential including the strongly directional character of the semiconductor interaction, and the Stillinger-Weber potential [34]. Our results on Lennard-Jones systems demonstrate that the pyramid-like structure formation is not specific for systems with covalent nature of the interatomic interaction.

Though Lennard-Jones pyramids can not be used for solid semiconductors, the investigation of the self-organization processes in the simple Lennard-Jones model allows to understand the nature of pyramid-like structure formation processes in systems with more complex interatomic interaction. Particularly, the above mentioned correlation between geometrical parameters of pyramids and the wetting behavior seems to have general nature for Lennard-Jones and semiconductors islands.

It is also worth to discuss an interesting and not mentioned before relationship between the pyramid-like structure formation and specific features of the nanodroplet spreading. Layered ("terraced", pyramid-like) but dynamical structures were discovered in laboratory experiments by Cazabat *et al.* [35, 36]. So, pyramid-like structures under discussion may be treated as frozen layered structures arisen during the droplet spreading.

Our results on the self-organization processes in systems composed of a rigid rod-like molecules are in agreement with one of the self-organization principles by Lehn [3]. According to this principle, the self-organization processes are more probable in systems composed of complex molecules. The linear rod-like conformation is of interest in view of many natural and technological systems. For example, polymer molecules used for the production of heat-resistant fibers are of this type [37]. Obviously, such sort of molecules may be used to produce heat-resistant nanostructures.

Using heterogeneous (structured) surfaces seems to be an important designable factor of the structure formation during the droplet spreading. Structures formed on heterogeneous surfaces reproduce, to a great or less extent, their own morphology. However the resemblance could not be perfect. As the wetting behavior is influenced by the structure of heterogeneous surfaces, there can be an indirect influence of the structured surface on the structures formed in the droplet spreading. Particularly, the mentioned above high-energy net of very low relative area promotes the pyramid-like structure formation during the droplet spreading concurrent with the crystallization.

7. Conclusion

1. Our computer simulation results have revealed many common features of the nanoscale and macroscopic spreading. Particularly, the wetting of solid surfaces by own melt droplets is characterized by the equilibrium contact angle 20–30° in both cases. The validity of the macroscopic Cassie law for the nanoscale spreading on heterogeneous surfaces with higher concentration of low-energy species may be treated as another confirmation of the general nature of many laws of the macroscopic and nanoscale spreading.
2. At the same time, some processes, e.g., the pyramid-like structure formation can occur in the nanoscale systems only.
3. The pyramid-like structure formation processes are not specific for covalent systems, particularly for Ge islands on Si substrates, but can be also observed in Lennard-Jones systems. The self-organization patterns in simple enough systems are of special fundamental and applied interest as these patterns can help to reveal the self-organization mechanisms in more complex systems.
4. Our molecular dynamics results on Lennard-Jones systems show that pyramid-like structures can be obtained not only by heterogeneous condensation processes (Stranski-Krastanow processes) but also using the nanodroplet spreading concurrent with the crystallization.
5. The probability of the self-organization is growing when the spreading droplet consists of multiatomic molecules. We have found that the effects of the liquid crystal ordering and the cluster structuring are most pronounced when the spreading droplet consists of rigid rod-like molecules.
6. The morphology of the heterogeneous substrate seems to be one of the most important designable factors influencing the structure formation processes during the droplet spreading.

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