COMPARATIVE MOLECULAR DYNAMICS STUDY OF SPREADING MECHANISM IN MOLECULAR AND METAL SYSTEMS

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ABSTRACT

A comparative study of simple and polymer Lennard-Jones (LJ) liquid droplet spreading as well as the spreading of lead on copper faces was carried out using the isothermal molecular dynamics. To investigate the spreading mechanism in LJ systems the labeled atom (monomer) technic was used. It was found that a single mechanism is not adequate to the simple LJ droplet spreading, but in general the rolling motion mechanism is most adequate for this case. The polymer droplet spreading involves a special mode of the slippage along the substrate, i.e. a special mode of the chain reptations. In the Pb/Cu systems we observed the pseudopartial wetting, i.e. a pronounced precursor monolayer and the following formation of the equilibrium droplet configuration with non-zero value of the equilibrium contact angle. The precursor layer formation was interpreted as a special case of the slippage of atoms along the substrate.

In memory of Prof. B.D. Summ (1933-2005)

INTRODUCTION

Spreading of liquid droplets over solid surfaces is a phenomenon interesting from both fundamental and applied viewpoints [1-3]. One of the early experimental studies on this topic was performed by Tanner [4]. Experimental results on the macroscopic droplet spreading are reviewed in [5]. The most important fundamental aspect of spreading relates to the problem of the triple line (wetting perimeter) motion which contradicts to the no-slip condition assumed in classical hydrodynamics. Different approaches were proposed to eliminate this contradiction [6]. The earliest, namely ‘the caterpillar track’ or ‘the unrolling carpet’ mechanism was proposed by Frenkel [7], Gegusin and Ovcharenko [8]. Later this mechanism was referred to as ‘the rolling motion mechanism’ [9]. According to this mechanism, liquid advances on the unwetted solid area like a caterpillar track with no contradiction to the hydrodynamic no-slip condition. Later, in 80th, the rolling motion mechanism was rejected by most scientists in favor of the slippage mechanism, which explains the spreading in terms of the slippage of molecules along the substrate in directions of spreading [10]. Among other alternative spreading mechanisms were proposed to resolve the contact line motion problem. The most known are the kinetic adsorption/desorption [11] and Cahn-Hillard-van der Waals [12] models. De Gennes [13] and Starov [14] introduced a new geometric model of the spreading droplet consisting of the main (bulk) area, the flat quasiequilibrium wetting layer and a transitional area between them. In the two last areas the disjoining pressure should be taken into account. Later, de Gennes developed the model under discussion in terms of the precursor layer formation [1].

The slippage model seemed to fail under the influence of interesting experimental results by Dussan [15] who injected microscopic dye particles into the wetting perimeter region and did not observe their sliding along the solid substrate. In review [1], de Gennes referring to the Dussan results tried to stop the long discussion on the spreading mechanism making a conclusion that simple (non-polymer) liquids spread following to the rolling motion mechanism whereas polymer liquids spread due to the sliding of molecules. However, the no-slipping of the dye particles seems not to be quite equivalent to the rolling motion of liquid at the wetting perimeter.
Besides, if the sliding of polymer molecules really takes place, the type of the slipping motion remained unclear.

In our paper [16] a comparative study of simple and polymer liquid spreading was carried out using isothermal molecular dynamics. To investigate the spreading mechanism the labelled atom technique was used. It was found that a single mechanism is not quite adequate to the simple nanodroplet spreading but in general the rolling motion mechanism is most adequate to the spreading of simple fluids. In turn, polymer droplet spreading involves a special mode of the chain reptation i.e. of their crawler-like slippage along the substrate.

For the last decade we study the spreading in metal systems. On the one hand, even single-component metals should be considered as binary systems consisting of the ionic skeleton and the electron gas. On the other hand, metal systems can be adequately described by one of the many body potentials which take into account all the terms into the interatomic interaction: ion-ion, electron-ion and electron-electron ones. And from this point of view, metal melts can be also treated as a special case of simple liquids. Therefore, the spreading in metal systems could be expected to follow the rolling motion mechanism. However, our MD results presented in this paper show that in some cases the spreading in metal 1 (melt droplet) / metal 2 (solid substrate) systems may be interpreted in terms of the slipping of atoms along the substrate. We mean Me1/Me2 systems which can be interpreted in terms of the pseudopartial wetting (PPW). PPW is an interesting but disputable phenomenon and corresponds to the case of the partial wetting when a droplet forms a nonzero equilibrium contact angle not on the dry solid surface but on the top of a precursor monolayer.

Up to the present time, there is a number of experimental and theoretical results [17] as well as the results of computer experiments [18, 19] confirming the existence of PPW as a special phenomenon in the case of the nonreactive spreading of molten metals on metal solid surfaces. At the same time, direct experimental studies are absent where the precursor layer formation during spreading of a metal droplet over the surface of another solid metal were observed. Really, in [17, 20] an experimental snapshot of a lead film on the Cu (111) face with Pb droplets on the film top is shown which demonstrates PPW. However, this film was not obtained via the spreading process: a Pb thick film was first deposited on Cu surface by evaporation and recondensation; then the sample was heated above the Pb melting temperature, and Pb drops were formed on a Pb layer via the dewetting process. The scanning Auger microprobe (SAM) was, finally, applied not to the liquid but to the solid Pb films containing frozen Pb droplets on its top. The results obtained in [1] seem to be of great interest. The high enough accuracy of SAM is, in particular, worth to be mentioned: the detection limit (sensitivity) of SAM was 0.01 Pb monolayer (ML). In our molecular dynamics (MD) experiments discussed below we observed the spontaneous precursor formation during the lead droplet spreading on copper faces (100) and (111).

**METHOD OF SIMULATION**

In our previous papers [16, 21, 22], the spreading of Lennard-Jones (LJ) droplets was simulated using both MD and Monte Carlo methods. We have used our program for the isothermal MD simulation of the evolution of Lennard-Jones and metal nanoparticles in the force field of the solid substrate involving the Verlet velocities algorithm and the Berendsen thermostat [23]. The shape of the starting drop corresponded to a sphere of initial radius \( R_0 \) with its center located at the distance \( R_0 + a_l \) 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 LJ pair potential

4-11
\[ \Phi(r) = 4\varepsilon_{sl} \left[ \left( \frac{a_{sl}}{r} \right)^{12} - \left( \frac{a_{sl}}{r} \right)^{6} \right], \]  

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

\[ \mu^*(z^*) = \frac{\mu(z)}{4\varepsilon_i} = \frac{D}{z^{3/2}} - \frac{C}{z^{3/2}}. \]

of the LJ solid substrate interpreted as a continuous half-space. In (1) \( r \) is the interatomic distance, \( \varepsilon \) and \( a \) are the energetic and the linear parameters of the pair potential, respectively. It is convenient to express \( \varepsilon_{sl} \) 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 \((\varepsilon_i, a_i)\) and solid \((\varepsilon_s, a_s)\) subsystems: \( \varepsilon_{sl} = \sqrt{\varepsilon_s \varepsilon_i} \), \( a_{sl} = \left( a_s + a_i \right)/2 \). Then, \( z^* = z/a_i \) is the reduced coordinate (the \( z \)-axis is normal to the solid interface), \( C \) and \( D \) are the attraction and repulsion constants, respectively. In particular, \( C = \pi n_s a_i^3 (\varepsilon_i/\varepsilon_s)^{1/2}/6 \) [21]. Varying the ratio \( \varepsilon_s/\varepsilon_i = \varepsilon_s^* \), we can reproduce cases of low-energy \((\varepsilon_s^* = 0.5 – 2)\) and high-energy \((\varepsilon_s^* = 5 – 50)\) substrates.

MD and Monte Carlo evolution in LJ systems was studied in dependence on the reduced temperature \( T^* = kT/\varepsilon_i \) (\( k \) is the Boltzmann constant). The value \( T^*_m = 0.65 \) corresponds to the macroscopic melting temperature of LJ liquids. For LJ systems the reduced time \( t^* = t/t_0 \) was used, where \( t_0 = \sqrt{\varepsilon_i/ma_i^2} \) is the time scale, determined by \( a_i \), \( \varepsilon_i \) and the mass \( m \) of an atom or of a monomers.

For metal nanoparticles the initial droplet configuration corresponded to a relaxed spherical fragment of the fcc lattice. Interatomic interactions in metal (droplet-substrate) systems were described by the tight-binding potential [24]. Then, for metal systems we did not use the reduced temperature and time. Computer experiments on Me1/Me2 systems were performed at temperatures \( T \) above the particle melting temperature \( T_m \). The problem of the size dependence of the melting temperature of metal nanoparticles is discussed in our papers [25].

**MD RESULTS FOR MOLECULAR SYSTEMS**

As was already mentioned, to study the spreading mechanism, we used an approach called the labeled (dyed) atom technique [16], which may be treated as a nanoscale analogue of Dussan’s method [15]. In our approach, some atoms or interacting centers in the spreading droplet were marked by different colours so that their motion can be observed during the nanodroplet spreading.

Snapshots of a simple nanodroplet, consisting of 3000 atoms, during the spreading on a low-energy substrate are shown in Fig. 1. In this case, an internal and arbitrary chosen atomic cluster was labeled by the black colour. One can see that a noticeable slippage of the labeled atoms along the substrate in radial directions was not observed. Some labeled atoms were evaporated. The contribution of evaporation into the spreading can vary for different droplets with the same initial parameters. So, the evaporation of some atoms from the droplet meniscus followed by recondensation on the substrate before the contact-line plays a certain role in spreading of simple nanodroplets. Some local clusters consisting of about a dozen atoms fell on the substrate as a whole from the droplet meniscus. This effect may be also considered as one of spreading mechanisms resembling to the rolling motion. We have also observed a slippage of labeled atoms along the droplet meniscus towards the solid surface. Presumably, such a surface flow may be considered as a specific Marangoni effect at the triple line. However, interpretation
of the nanoscale spreading in terms of gradients of surface and line tensions, i.e. in terms of the typical Marangoni effect, seems not to be correct.

The kinetic dependence (Fig. 2) for the reduced value $r_i^* = r_i / a_i$ of the first monolayer radius $r_i$ versus the reduced time $t^*$ presented in logarithmic variables demonstrates different subsequent spreading regimes, among them the regime corresponding to $r_i \sim \sqrt{t}$ noted first in [26, 27] for quasiplanar oligomer droplets.

The results for spreading of macroscopic droplet are usually presented by the power law [1–5]

$$r_p = At^n$$

(3)

where $A$ is an individual constant of the droplet depending on its volume. During the macroscopic droplet spreading, the following consecutive regimes are usually observed: kinetic ($n = 1$), internal ($n = 0.5$) and viscous ($n = 0.1$) for the case of incomplete wetting [3]). Figs. 1–2 correspond to the case of incomplete wetting. It is remarkable that the initial regime of nanodroplet spreading is described by $n = 0.8$, which is close to unity. The final regime is characterized by the same value $n = 0.1$ of exponent $n$ as the macroscopic viscous regime.

Fig. 1. Subsequent configurations of a simple LJ spreading droplet on the low-energy substrate with $\varepsilon^* = \varepsilon_s / \varepsilon_i = 0.5$: (a) $t^* = 0$, (b) $t^* = 50$ and (c) $t^* = 100$. 

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Fig. 2. Simple nanodroplet spreading kinetics in the case of incomplete wetting ($\varepsilon^*_i = 0.5$).

However, for nanodroplets the intermediate regime ($n = 0.5, r_i \sim \sqrt{t}$) does not correspond to the inertia effect but to the surface diffusion from an unlimited source.

Fig. 3. Snapshots of the octamer droplet on high-energy LJ substrate with $\varepsilon^*_i = 5$: (a) $t^* = 0$, (b) $t^* = 100$ and (c) $t^* = 160$.

For polymer systems, all the interacting centers of some modeling chain-like molecules were also labeled by a different colour (black in Figs. 3 and 4). Computer experiments were carried out for systems presented by tetramers (p=4), octamers (p=8) and hexadecamers (p=16). Each segment of such a modeling chain may be interpreted as the Kuhn segment of a flexible polymer.
chain. Snapshots of a single chain during its motion on the high-energy substrate, presented in Fig. 4, demonstrate that chains slip (crawl) along the substrate in a radial direction.

However, it is a very special kind of the slipping: in reality the chains move along the substrate-like crawlers or worms being subsequently compressed and stretched. A similar motion of a chain among others (i.e. in an imaginary tube) is referred to as the reptation in physics of bulk polymers [28]. Thus, the mechanism of spreading of droplets consisting of chain-like molecules relates to the chain reptation along the substrate.

**ON SPECIFIC FEATURES OF THE DROPLET SPREADING IN METAL SYSTEMS**

In this paper the spreading of a metal droplet (Me1) on the solid surface presented by the same or other metal (Me2) will be considered. The spreading in Me1/Me2 systems can be divided into non-reactive and reactive cases. In the last case the formation of intermetallics plays an important role in the droplet-substrate interactions. For instance, the reactive wetting controlled, to a greater or lesser extent, by chemical reactions in Al/Ni systems was studied in [29]. The reactive spreading is a much more complicated pattern of the droplet spreading for both direct and computer experiments. In what follows the basic case of the non-reactive spreading in metal systems will be discussed. In turn, PPW phenomenon seems to be the most interesting and, at the same time, disputable specific case of the non-reactive spreading in metal systems. PPW was defined [17-20] as a kind of the partial wetting when the equilibrium or quasiequilibrium droplet configuration with a finite value of the equilibrium contact angle $\theta_e > 0$ is formed not on the dry solid surface but on the top of a film presented by the same substance as the spreading droplet.

On the one hand, PPW phenomenon is reasonably enough justified in the above papers. On the other hand, an opinion of some scientists should be noted that there are no reasons to consider PPW as a special case of the partial wetting as an adsorption layer is always observed even on hydrophobic surfaces. However, such a layer does not always play an important role in the spreading and wetting phenomena. Besides, the term ‘adsorption layer’ usually proposes an equilibrium mono- or polmolecular layer formed after the evaporation of the droplet molecules and their following recondensation on the substrate whereas PPW is usually associated with other ways of the monolayer formation on the solid surface (see introduction). In [17] for Pb/Cu systems PPW was observed on both (100) and (111) faces. In [18] PPW of copper by lead droplets was simulated using MD and the embedded atom method. According to [18] on face (111) a noticeable spontaneously formed precursor bilayer was observed during the lead droplet spreading, as well as the final droplet configuration with a finite equilibrium contact angle...
\[ \theta_0 > 0. \] Respectively this case of the partial wetting was interpreted as PPW. On face (100) of copper a precursor mono- and bilayer was not observed. So, PPW seems to be sensitive, many-sided and disputable phenomenon. The goal of our MD experiments on Me1(droplet)/Me2(substrate) systems is to elucidate some laws and mechanisms of this phenomenon.

**MD STUDY OF THE LEAD DROPLET SPREADING ON THE COPPER SURFACE**

Taking into account that Pb(l)/Cu(s) systems were studied earlier [17, 18, 20, 30], we simulated the spreading of lead nanodroplets on the copper surface (faces (100) and (111)) using isothermal MD and the tight-binding potential [24], i.e. another many-body potential in comparison with [18]. The droplet spreading should be investigated at \( T \geq T_m \), and the nanoparticle melting temperature \( T_m \) depends on the particle size, i.e. on the number of atoms \( N \) the particle consist of. Therefore, we first investigated the size dependence of \( T_m \) for free lead nanoparticles. Method of the determination of \( T_m(N) \) dependence is described in our paper [25] where the \( T_m(N) \) dependence was investigated for gold, nickel and aluminum nanoparticles. Unfortunately, values of \( T_m \) obtained for Pb particles using the tight-binding potential (Fig. 5) are overestimated (the melting temperature \( T_m^{(C)} \) of the bulk Pb is 600K). However, this problem is not principal for comparison of MD results on wetting and spreading with experimental data for macroscopic systems if these data are compared for the same relative temperatures \( T/T_m \). In particular, we can compare values of \( \theta_0 \) obtained at \( T = T_m \) (MD) and \( T = T_m^{(C)} \) (direct experiments).

![Fig. 5. Size dependence of \( T_m \) for Pb nanoclusters.](image)
Table

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<th>Source</th>
<th>$N$</th>
<th>$T / T_m$</th>
<th>$\theta_e$, deg</th>
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<th>face (111)</th>
<th>polycrystalline substrate</th>
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Contrary to [18], in our MD experiments and in MD experiments [31] PPW was observed on both (100) and (111) copper faces (Fig. 6). And it is noteworthy that the droplet spread on a precursor monolayer advancing the spreading of the whole droplet. In our computer models the precursor covered all the bottom of the simulation cell, and the equilibrium droplet configurations (Fig. 6) were formed on the top of the equilibrium monolayer which in turn may be treated as the final state of the dynamic precursor layer. The values of the equilibrium contact angle $\theta_e$ obtained in our MD experiments satisfactorily agree with the available experimental macroscopic data and MD results of other authors (see Table). However, it is a bit surprising that in [17] the more dense face (111) is characterized by a greater value of $\theta_e$.

So, the results of our MD experiments on modelling Pb(l)/Cu(s) systems show that PPW phenomenon, relating to the precursor monolayer formation and its principal role in the partial wetting ($\theta_e > 0$). In [17] the sensitivity of the phenomenon in question was also noted concerning corresponding experimental data: small variations of the Me1/Me2 system parameters can principally transform the spreading scenario from pseudopartial to partial or complete wetting.

CONCLUSION

So different mechanisms can be involved in the droplet spreading, including different variants of the molecule (atom) slippage. The simple LJ droplet spreading corresponds to the rolling motion mechanisms, and the slippage of atoms along the substrate is not noticeable and principal for the spreading in these systems. At the same time, discussed above PPW in Me1/Me2 systems corresponds to the precursor monolayer formation by means of the slippage of the droplet atoms along the substrate. Obviously, if the simulation cell bottom were not restricted, the lower monolayer spreading would continue up to the island monolayer formation i.e. resulted in the complete wetting. Of course, PPW associated, as was shown above, with the precursor layer formation is not typical for all Me1/Me2 systems. For example, in [32] we
studied the spreading of copper nanodroplets on face (100) of nickel. And for this system we do not observe any precursor: radii of 3 lower monolayers were close to each other during all the spreading process. So, just the slippage mechanism in Me1/Me2 systems results in the spontaneous precursor monolayer formation.

In the case of polymer or oligomer droplets the spreading involves a very special kind of the slippage of chain-like molecules i.e. their reptations along the substrate. Unfortunately there are no direct experimental evidences either of the chain reptations during the polymer droplet spreading or of the possibility of the precursor monolayer formation in Me1/Me2 systems in the case of PPW.

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REFERENCES