

Molecular Dynamics Simulation of Microscopic Droplet Spread on Rough Surfaces

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This study uses molecular dynamics simulations to elucidate the spreading behavior of a liquid droplet on a rough solid surface. The Lennard–Jones potential energy model is adopted as the interaction model between the liquid and the solid molecules. The paper considers two types of rough surface: periodic and random. These surfaces are characterized by their roughness height and their spatial variation. For a periodic surface, the roughness height is defined by the amplitude, A , while for a random surface, it is defined in terms of the standard deviation of the roughness height, σ . Regarding the spatial variation of the surface, a periodic surface is characterized by the wavelength, λ , while the random surface is characterized by its autocorrelation length, L . Simulation results indicate that the characteristics of the rough surface can significantly influence spreading behavior, in terms of final equilibrium time, spreading radius, and spreading topography. It is observed that the effects of roughness height and spatial variation are broadly similar for both periodic and random surfaces. It is found that increasing roughness height and decreasing spatial periodicity both prolong the final equilibrium time, and that the final spreading radius decreases with increasing roughness height and increases with larger spatial periodicity.

KEYWORDS: spreading, rough surface, molecular dynamics simulation

§1. Introduction

The spreading dynamics of a liquid on a solid surface are determined by different physical and chemical disciplines. Surface wetting occurs in many practical processes, *e.g.* surface coating, casting, laser cutting, floating screening, rubbing, adhering, lubrication, interface active agent and capillary action. Due to extensive applications, the spreading of a liquid on a solid surface has been, and continues to be, the subject of considerable research efforts, both theoretically and experimentally.^{1–12)}

In conventional macroscopic theory, the three-phase equilibrium contact angles, which exist between the liquid droplets, the solid surface and the air, can be determined by Young's equation. In this way the motion trend of a droplet spread may be observed qualitatively. However, if droplets spread on a solid surface which has a non-slip boundary condition, a contradiction occurs since this boundary prevents movement of the contact line between the solid and the liquid. Dussan *et al.*¹³⁾ suggested that droplet spreading could be attributed to a rolling mechanism. Marmur and Lelah^{14,15)} investigated the wetting phenomenon of water, ethanol, and a surface-active agent on smooth solid surfaces such as glass plates. From both static and dynamic studies, de Gennes¹⁶⁾ contended that the wetting phenomenon occurs due to a droplet-spreading process, in which the condition of a solid surface changes from a completely dry state to a partially wet one, and then finally to a completely wet state. Teletzke *et al.*^{17,18)} further examined the spreading of liquid on a solid surface, and indicated that the mechanical process of droplet spread-

ing comprises of three stages: primary spreading, secondary spreading, and bulk spreading. Heslot *et al.*^{19–21)} investigated the spreading mechanism of a PDMS (polydimethylsiloxane) droplet on a solid plate by adopting an experimental method. According to their results, the spreading front is formed by a fairly flat mono-molecular layer, which moves outward at a constant speed and which is known as a precursor film. De Gennes²²⁾ demonstrated that the growth rate of the precursor film radius is proportional to $\sqrt{t}$. Abraham *et al.*^{23,24)} adopted statistics mechanics and Langevin's equation to establish a solid-on-solid (SOS) physical model of spreading and wetting, which could be used to analyze the dynamic contact angles and two-dimensional development structure of a precursor film. Chakrabarti²⁵⁾ verified the accuracy of the SOS model by employing a numerical method. Ehrhard *et al.*²⁶⁾ further examined the effects of gravity and temperature on droplet spreading. By adopting statistics mechanics, Lukkarinen *et al.*²⁷⁾ developed a model, known as the Ising's Physical Model, to explain the droplet-spreading behavior, again verifying that the growth rate of the precursor film radius is proportional to $\sqrt{t}$.

Molecular dynamics (MD) theory has recently been applied extensively to droplet-spreading behavior. Yang *et al.*^{28,29)} performed a systematic MD study of a simple liquid on a smooth solid surface, in which the droplet-spreading behavior was controlled by changing the values of the solid-liquid and liquid-liquid attraction potential. According to their findings, a two-layered droplet structure appears in some circumstances, and the spreading profile of the droplets on the flat plate becomes step-like (terraced spreading). In this situation the

growth rate of the precursor film radius $R(t)$ is proportional to $\sqrt{\log t}$. Notably, this relationship differs from the above $R(t) \sim \sqrt{t}$. Nieminen *et al.*³⁰⁾ suggested that $R(t)$ is proportional to $\sqrt{t}$ in the case where the temperature of the liquid molecules is controlled by application of the Nose-Hoover's isothermal theorem and the solid surface is regarded as a slippage boundary. However, this argument appears questionable since the system composition is actually inhomogeneous, and the solid surface is in fact a non-slip boundary. For this reason, Yang *et al.*²⁹⁾ contended that $R(t)$ is also affected by the number of liquid-droplets molecules, somehow accounting for the difference between experimental outcomes and MD simulation results.

From a microscopic perspective, no perfectly smooth solid surface exists. Despite the aforementioned developments, droplet spreading on rough surfaces using molecular dynamics simulations has seldom been studied. Regardless of efforts made to reduce surface roughness during manufacturing, it is impossible to totally eliminate the many cavities and surface irregularities of different scales which appear on a solid surface. The resulting undulating profile obviously affects the spreading dynamics of the droplets on the surface. This paper performs molecular dynamics simulations to examine the spreading behavior of liquid droplets on two types of rough surfaces under isothermal and non-gravity conditions. Results from this study provide insights at a microscopic level into droplets spreading on a rough surface.

§2. Numerical Modeling

Investigating the spreading behavior of liquid droplets on a rough solid surface involves three tasks: generation of a rough surface, representation of the droplets and the rough solid region by several molecules, and the performance of MD simulations. This paper considers two types of rough surfaces: periodic and random. A rough surface can be characterized by its roughness height and spatial variation, while a periodic rough surface is generated as a sinusoidal surface with given values of amplitude A and wavelength λ . Both surfaces are normalized according to the molecular radius, δ . A method proposed by Patir³¹⁾ is used to generate random surfaces with a prescribed autocorrelation function and surface height distribution. The autocorrelation function is a process by which the relationship between any point on the surface profile and all other points is determined. It describes the extent to which a surface roughness pattern repeats. The autocorrelation length, defined as the length at which the autocorrelation function becomes zero, is a typical parameter used to characterize the spatial variation of a random surface. Hence, a generated random surface can be defined by the standard deviation of its roughness height σ , and the autocorrelation length L .

Once the desired rough surface has been generated, the corresponding rough solid plate comprises two portions of solid molecules. In all the cases examined, it was found that the lower portion contained three (molecular) layers of molecules ($40 \times 40 \times 3 = 4800$),

and that the upper portion consisted of a number of molecules forming the desired surface profile. A liquid droplet (radius = 11.97δ) consists of 1372 molecules, which had been set in equilibrium from an initial F.C.C. configuration through a preceding run of Molecular Dynamics. Immediately prior to commencing the spreading process, the center of the droplet is located directly above the midpoint of the solid plate, with its lowest point almost in contact with the top profile of the solid plate.

In the molecular dynamics simulation of a microscopic system, the interaction between molecules is represented by a potential energy function. The function which is most frequently used is the Lennard-Jones potential energy function. This function is representative of the general features of the true intermolecular potential energy since it contains terms describing both the steep repulsion branch and the long-range attraction characteristics which exist between the molecules. Although the Lennard-Jones potential is a simplified model, it does nevertheless have much in common with more detailed models, and has a clear advantage in terms of its computational simplicity. Therefore, it is often used as a generic potential for qualitative explorations which don't involve specific substances. In this study, a 12-6 Lennard-Jones potential is used to describe the interaction between the molecular system under consideration. The system is bounded, but spatially homogeneous. In other words, the system is bounded but free of physical walls, and so the system may be described by the periodic boundary conditions. Five periodic boundaries are set, i.e. along the top surface and the four vertical faces of the analysis domain. Figure 1 depicts the initial geometry, and subsequent spreading snapshots, of two identical liquid droplets, on two (generated) rough solid surfaces. Figure 1(a) represents a periodic profile of $A = 3$ and $\lambda = 2\pi$, while Fig. 1(b) shows a random profile of $\sigma = 2$ and $L = 5$.

In the 12-6 Lennard-Jones potential energy function, the liquid-liquid potential ratio $d_{ll} = 1.0$, and the solid-liquid potential ratio $d_{sl}/d_{ll} = \alpha = 2.0$. The Gear's five step, predictive-corrective method is used to integrate

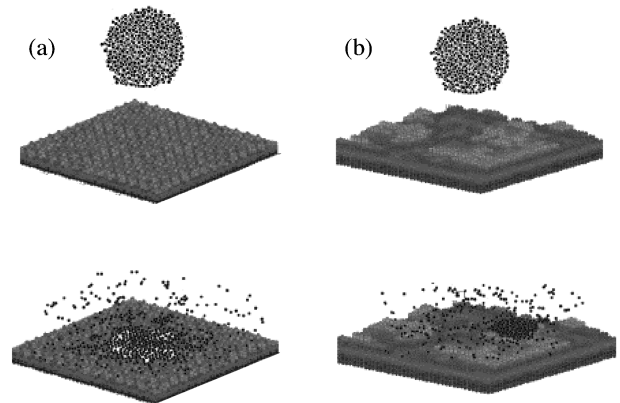


Fig. 1. Initial geometry and subsequent spreading snapshots of one liquid droplet on generated rough solid surfaces: (a) periodic ($A = 3$, $\lambda = 2\pi$); (b) random ($L = 5$, $\sigma = 2$).

Newton's equations of motion. This yields the time-history profiles of the coordinates and the velocity and acceleration vector of each molecule, from which the global macroscopic physical properties can be determined. The dimensionless temperature of the system $T^* = 0.7$, and the dimensionless time unit $\tau = t/\sigma\sqrt{m/\varepsilon}$. The total kinetic energy of the system (including all molecules) is adjusted throughout the entire simulation process so that it remains constant, thus satisfying the presumed isothermal condition corresponding to T^* . The spreading process of liquid droplets is monitored sequentially, and computation is continued until the spreading velocity of the droplets approaches zero, indicating that the system has reached its final equilibrium state. The simulation results are then used to compare the effects of different roughness parameters on droplet spreading characteristics, *e.g.* the final equilibrium time, the spreading radius, and the spreading topography.

§3. Results and Discussions

In this study, ten different rough solid surfaces were generated. Five of them corresponded to periodic rough surfaces with $(A, \lambda) = (1, 2\pi), (2, 2\pi), (3, 2\pi), (2, \pi), (2, 4\pi)$, and the remainder corresponded to random rough surfaces with $(\sigma, L) = (1, 10), (2, 10), (3, 10), (2, 5), (2, 20)$. Table I summarizes the number of molecules used to simulate the solid portion for each case, and the time steps required to reach the final equilibrium state. This section considers the spreading behavior of a 1372-molecule droplet on these various rough surfaces by molecular dynamics simulation. The outer boundary of the liquid droplets after spreading is defined as a cluster of particles with an inter-particle distance less than 1.4δ .

Figure 2 illustrates the spreading processes of such droplets on periodic rough surfaces with constant wavelength, $\lambda = 2\pi$, but different amplitudes, $A (= 1, 3)$. The points in these figures represent the centers of the molecules, where the three-dimensional system has been projected on the two-dimensional x - z plane. According to the obtained results, the droplet-spreading rate changes significantly with variations in A . When the value of amplitude A is equal to 1, droplet-spreading reaches the final equilibrium state at $\tau_{\text{fin}} \approx 200$; meanwhile, at $A = 3$, τ_{fin} increases to about 380. This is due to the fact that the increase of A implies a greater variation in surface topography and, therefore, a larger surface-contact area at the same spreading radius. The results demonstrate that amplitude is an important system parameter for droplet spreading on a periodic rough surface. Figures 2(c) and 2(d) display the spreading

processes of the same droplets on periodic rough surfaces with constant values of amplitude, $A = 2$, but with different wavelengths, $\lambda (= \pi, 4\pi)$. These Figures show that the final equilibrium time τ_{fin} increases (from 200 to 560) with increasing wavelength λ , and it may therefore be inferred that wavelength is another important parameter in the droplets spreading process. The physical explanation for the results observed is that the increase of λ implies a decrease of the surface curvature, leading to a delay in the spreading of droplets toward the region outside the first crest zone encountered.

Figure 3 describes the spreading processes of the same droplets on random rough surfaces with constant autocorrelation length, $L = 10$, but with different values of standard deviation of roughness height, $\sigma (= 1, 3)$. According to the results obtained, the final equilibrium time τ_{fin} increases markedly (from 200 to 600) as the standard deviation of roughness height σ increases. This confirms that σ is an important system parameter for droplets spreading on random rough surfaces. As shown in Figs. 3(a) and 3(b), in contrast the case of periodic surfaces, a non-symmetric droplet-spreading topography appears, due to the initially non-symmetric rough surface. Figures 3(c) and 3(d) present the spreading processes of the same droplets on random rough surfaces with a constant standard deviation of roughness height, $\sigma = 2$, but with different values of $L (= 5, 20)$. These results indicate that for random surfaces, the effects of autocorrelation length on the final equilibrium time are less significant.

Figure 4 shows the time history profile of the maximum liquid height (above the average datum of the rough surface), H_{max} , for a plate and for various rough surfaces. Obviously, the final equilibrium time is shorter for the smooth plate than for any of the rough surfaces. Figure 4(a) summarizes the influence of relative amplitude on maximum liquid height during the spreading process. This Figure indicates that larger roughness heights lead to longer final equilibrium times for both periodic and random rough surfaces. Figure 4(b) presents H_{max} versus τ curves for rough surfaces with constant amplitude, $A (\sigma = 2)$, but different wavelengths, $\lambda (L)$. The relatively flat portion of the curve represents the period in which droplets spread from the trough to the crest. It can be postulated that the (resulting) droplet potential in a trough is substantially larger than when it is near a crest, and that the spreading rate of droplets toward a trough is therefore faster than that toward a crest. It should be noted that at the same values of $A (\sigma)$, the values of H_{max} at the

Table I. Summary of the number of molecules representing the solid plate.

λ/L		Periodic rough surface			Random rough surface		
		$A = 1$	$A = 2$	$A = 3$	$\sigma = 1$	$\sigma = 2$	$\sigma = 3$
Solid	$\pi/5$	5640	7243	8850	9510	17278	28858
	$2\pi/10$	5640	7247	8843	8522	14628	NON
Plate	$4\pi/20$	5640	7251	8841	7818	12210	NON

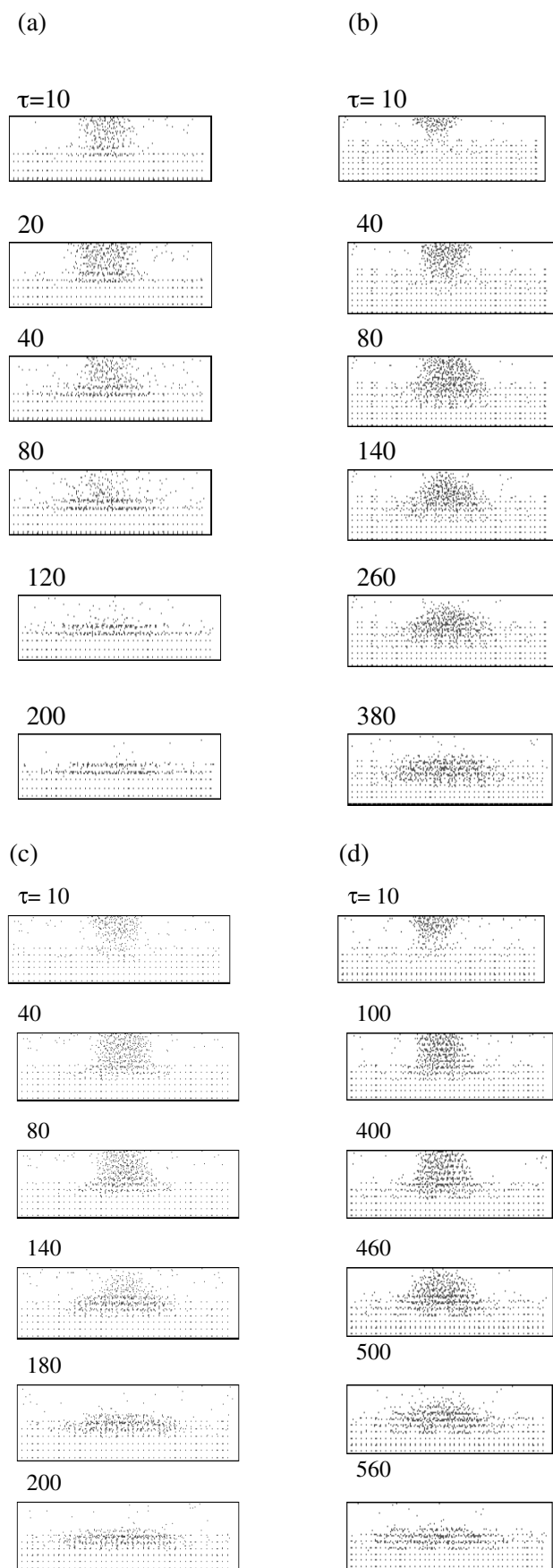


Fig. 2. Spreading processes of a droplet on periodic rough surfaces with $(A, \lambda) =$: (a) $(1, 2\pi)$; (b) $(3, 2\pi)$; (c) $(2, \pi)$; (d) $(2, 4\pi)$.

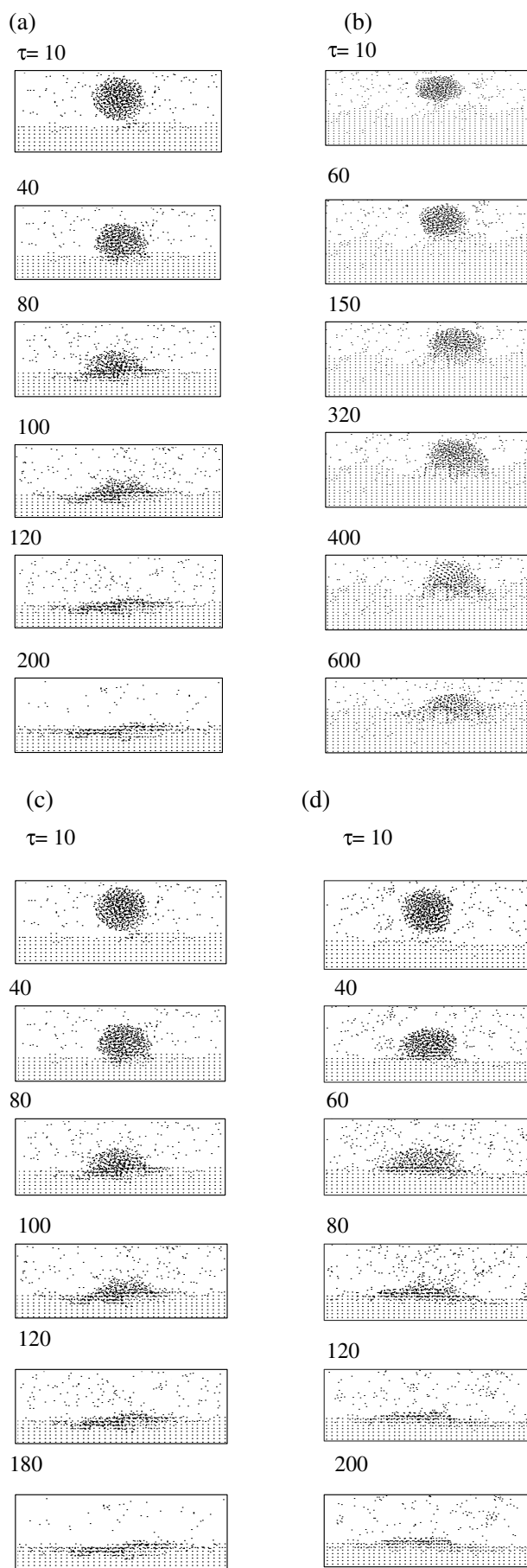


Fig. 3. Spreading processes of a droplet on random rough surfaces with $(\sigma, L) =$: (a) $(1, 10)$; (b) $(3, 10)$; (c) $(2, 5)$; (d) $(2, 20)$.

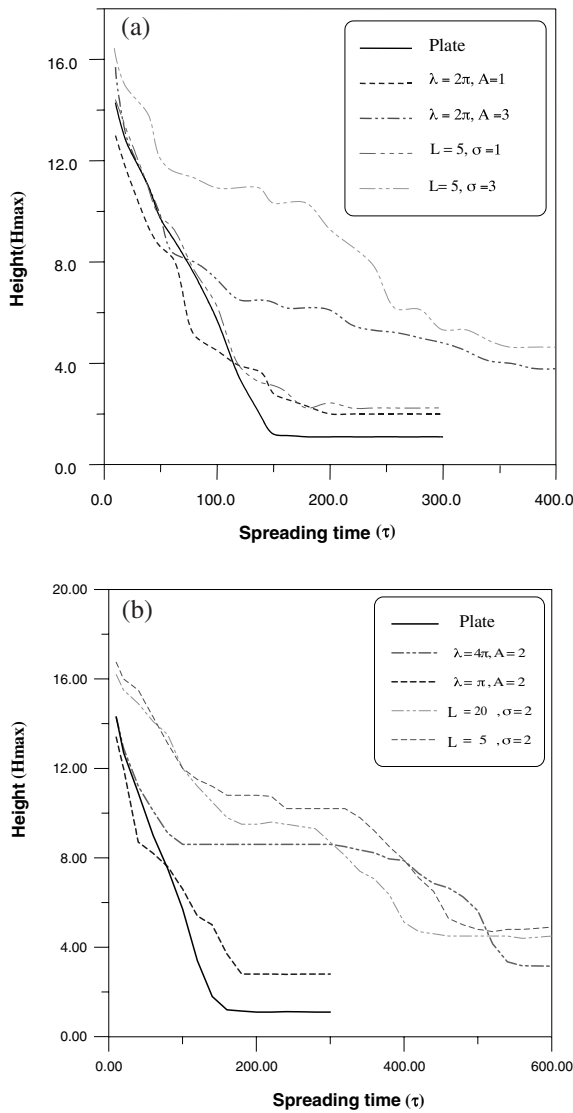


Fig. 4. $H_{\max}$ versus τ curves for rough surfaces with: (a) same $\lambda = 2\pi$ ($L = 5$) but different A (σ); (b) same $A = 2$ ($\sigma = 2$) but different λ (L).

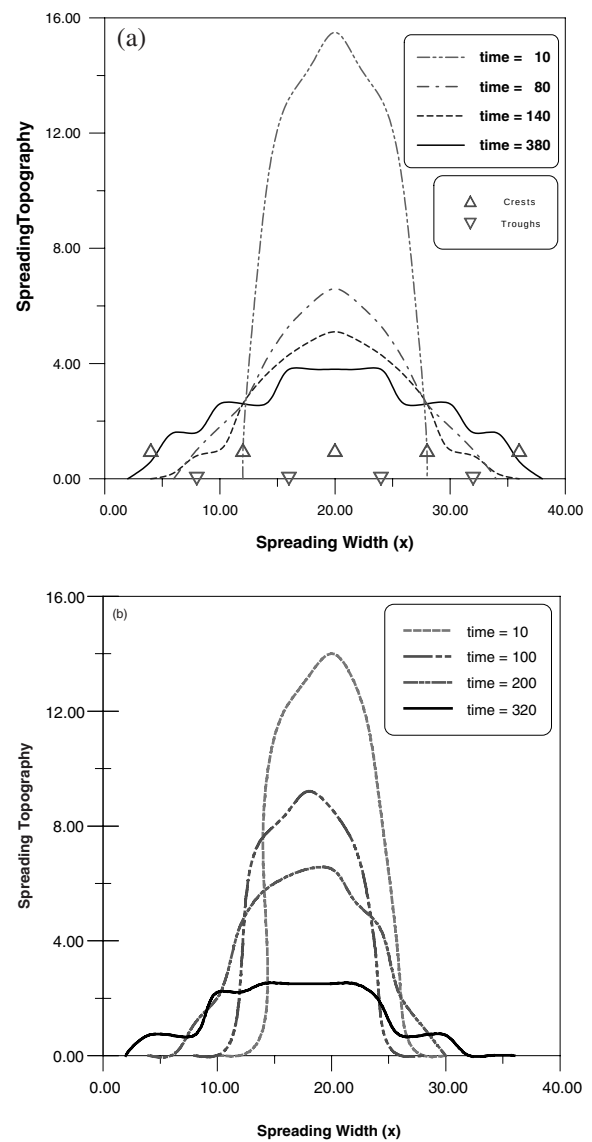


Fig. 5. Spreading topography of a droplets on rough surfaces of: (a) $A = 3$, $\lambda = 2\pi$; (b) $\sigma = 1$, $L = 10$.

final equilibrium state are very similar for different values of λ (L).

Figure 5 presents the spreading topographies of droplets on rough surfaces with $(A, \lambda) = (3, 2\pi)$ and $(\sigma, L) = (1, 10)$. It is observed that the liquid height gradually decreases with increased spreading time. If the center of the droplets is initially aligned perfectly with respect to one crest or trough of the surface, a symmetric spreading topography occurs for a periodic rough surface. For $(A, \lambda) = (3, 2\pi)$, a layered structure forms near the droplets front at $\tau \approx 140$, and terraced spreading in the form of a three-layered structure appears at $\tau_{\text{fin}} \approx 380$. This result is similar to the findings of Yang *et al.*²⁹⁾ for droplet-spreading on a flat plate. If the locations of the crests and troughs along the horizontal axis of Fig. 5(a) are considered, however, it will be seen that the occurrence and shape of the terraced spreading also depends upon the topographic profile of the rough surface. Figure 5(b) shows the spreading of droplets on a random rough surface. The presence of a

skew spreading topography will be noted due to the unsymmetrical nature of such a surface.

Figure 6 shows the final equilibrium topography of droplets for a plate and various rough surfaces. Clearly, droplets spreading on a plate yield the smallest values of $H_{\max}$ at τ_{fin} and the largest final spreading radius R_f . As shown in Figure 6, decreases in the roughness height (A or σ), or in the spatial variation, caused by larger values of λ or L , result in the final equilibrium topography of a rough surface approaching that of droplets spreading on a plate. As before, it may be observed that a symmetric final equilibrium topography is shown for a periodic rough surface, whereas a random rough surface exhibits a skew spreading topography. Some final equilibrium topographies also reveal the presence of the terraced spreading phenomenon.

The results shown in Figs. 6(a) and 6(b) indicate that surface roughness has a significant influence on the magnitude of the contact angle. In Fig. 6(a), the contact angle for a flat plate is approximately equal to, but

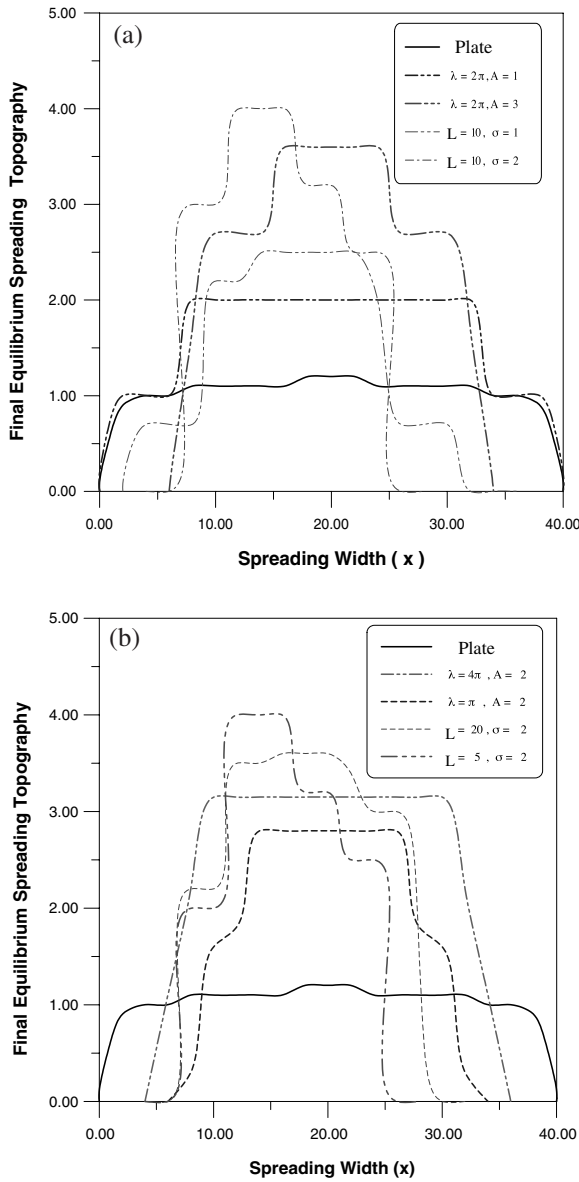


Fig. 6. Final equilibrium topography of a droplets on rough surfaces with: (a) same $\lambda = 2\pi$ ($L = 10$) but different A (σ); (b) same $A = 2$ ($\sigma = 2$) but different λ (L).

slightly less than 90° . However, the contact angle decreases for rougher surfaces. For example, the contact angle of a periodic rough surface with $(A, \lambda) = (1, 2\pi)$, is almost the same as for a flat surface. However, the contact angle of a periodic rough surface, $(A, \lambda) = (3, 2\pi)$, decreases slightly. The contact angle of a periodic rough surface is more significantly influenced by decreases of the wavelength, λ , as can be seen in Fig. 6(b) for the contact angle of $(A, \lambda) = (2, \pi)$. As seen in Fig. 6(a) and Fig. 6(b), the influence of the characterized parameters of the random rough surface, i.e. σ and L , on the change in contact angle is insignificant. However, the contact angle of the random rough surface is far less than that of the flat and periodic rough surfaces. This also indicates that the influence of random rough surfaces on the contact angle is more significant than that of periodic rough surfaces. The results obtained here are consistent with those obtained from the macroscopic viewpoint.³²⁾

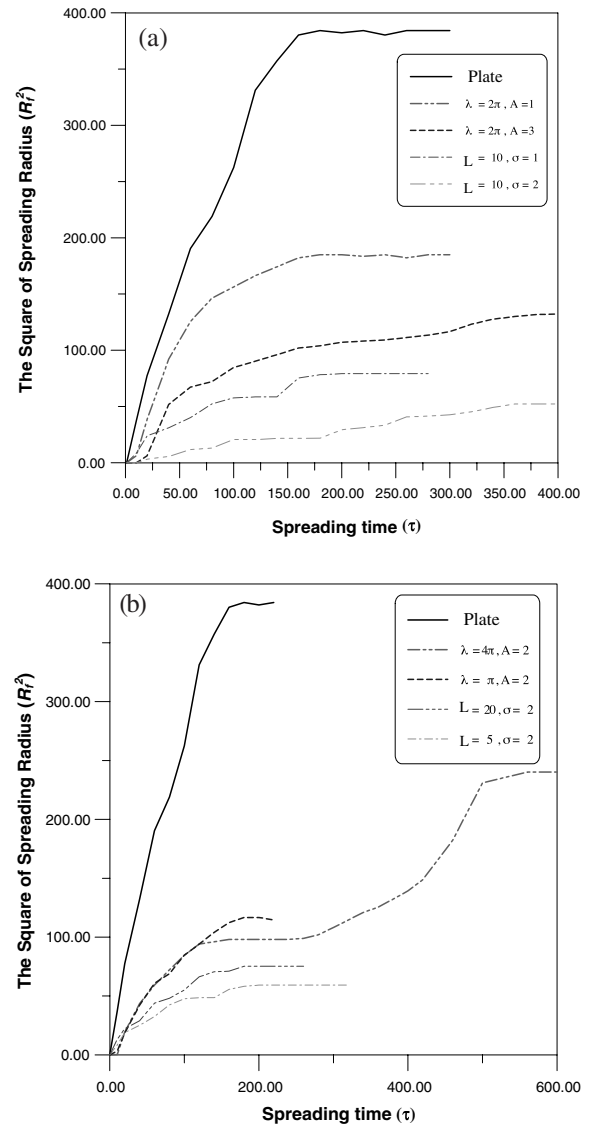


Fig. 7. Square of spreading radius versus τ curves for periodic rough surfaces with: (a) same $\lambda = 2\pi$ ($L = 10$) but different A (σ); (b) same $A = 2$ ($\sigma = 2$) but different λ (L).

It may be concluded that contact angles which are originally less than 90° decrease as surface roughness increases.³²⁾

Figure 7 illustrates the square of the spreading radius R^2 as a function of spreading time τ for a plate and for various rough surfaces. In general, it may be observed that the linear growth law ($R^2 \sim t$) of droplet-spreading on a plate is not valid for rough surfaces. The growth law for rough surfaces is highly non-linear, depending upon the roughness parameters, or the occurrence of terraced spreading. Figure 8 compares the values of the square of the final equilibrium radius R_f^2 for droplets spreading on a plate and for those spreading on various rough surfaces. The results indicate that the final equilibrium radius, R_f , decreases as the roughness height increases. Meanwhile, for a constant roughness height (A or a), it is found that the final equilibrium radius increases with decreasing spatial periodicity (longer period). Moreover, since a plate represents a surface with zero roughness

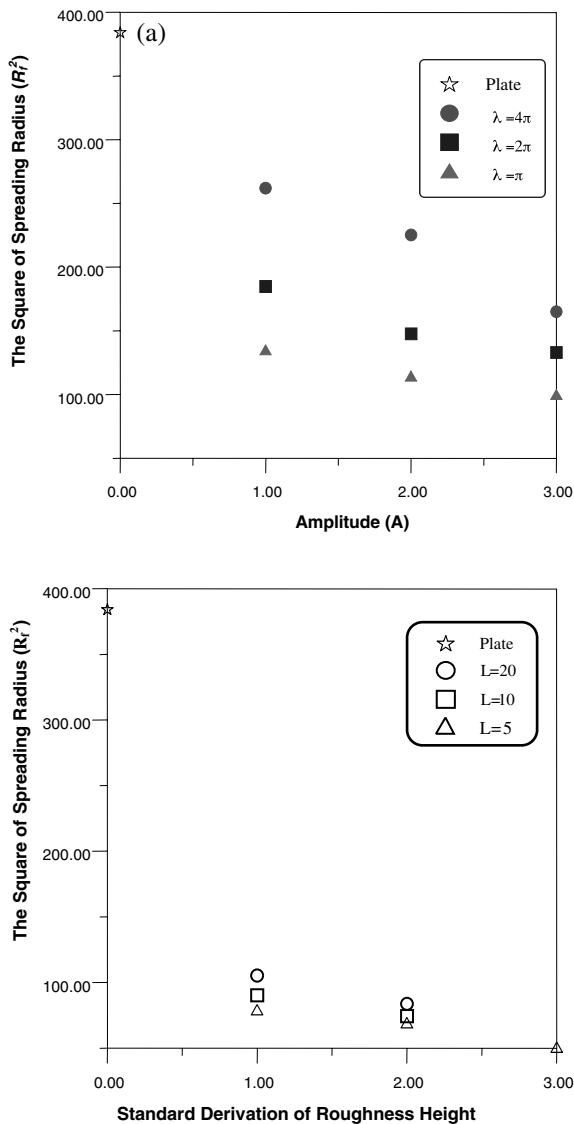


Fig. 8. Comparison between R_f^2 of a droplet on a plate and those on various rough surfaces.

height and spatial variation, its corresponding value of R_f is larger than that for any rough surfaces.

§4. Summary and Conclusions

All solid surfaces are microscopically rough to some extent, owing to the limitations of manufacturing precision and the nature of microscopic solid structures. This paper has investigated the spreading behavior of liquid droplets on two types of rough surface by performing molecular dynamics simulations. Two major characteristics of a rough surface are its roughness height and spatial variation. In this study, a periodic surface has been defined by its amplitude, A , and its wavelength, λ , while a random one has been characterized by the standard deviation of its roughness height, σ , and its autocorrelation length, L . For periodic rough surfaces, it has been determined that increasing the amplitude, A , or the wavelength, λ , both prolong the final equilibrium time, and that the final spreading radius decreases with increasing amplitude A , but increases with increasing

wavelength, λ . For random rough surfaces, it has been observed that the roles of the standard deviation of the roughness height, σ , and the autocorrelation length L somewhat resemble those of the amplitude, A , and the wavelength, λ , respectively. The agreement between the results for the two types of surface is reassuring, and provides further perspectives in elucidating the spreading behavior of liquid drops on a rough surface.

Acknowledgments

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