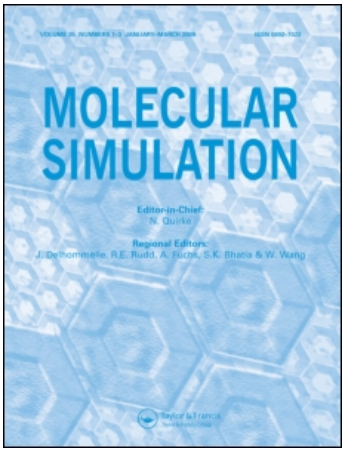

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Dissipative Particle Dynamics of the Thin-Film Evolution in Mesoscale

W. Dzwinel[a]; D. A. Yuen[b]
[a] Institute of Computer Science AGH, Kraków, Poland [b] Minnesota Supercomputer Institute and Department of Geology and Geophysics, University of Minnesota, Minneapolis, Minnesota, USA

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DISSIPATIVE PARTICLE DYNAMICS OF THE THIN-FILM EVOLUTION IN MESOSCALE

W. DZWINEL[a,*] and D. A. YUEN[b]

[a] *Institute of Computer Science AGH, Al. Mickiewicza 30, 30-059 Kraków, Poland;*
[b] *Minnesota Supercomputer Institute and Department of Geology and Geophysics, University of Minnesota, Minneapolis, Minnesota 55415-1227, USA*

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Computer simulation is an important tool for studying the dynamical behavior of thin films. The existing models of liquid film flows are based on the evolution equation (EE) and lubrication theory, which are approximations to the Navier-Stokes continuum equations. The validity conditions for these approximations and disadvantages of numerical schemes impose serious limitations on these continuum models. Thin liquid layers in nanoscale technology may exhibit microscale features, which cannot be described by using the EE equations. We propose new numerical models for falling film and falling sheet. They are based on the particle paradigm and the dissipative particle dynamics (DPD) method. DPD represents a system of mesoscopic-sized particles, which can interact *via* direct conservative, two-body potentials. The particles can exert friction and Brownian forces on each other. We consider two cases of fluid film flows for which the main driving force is the gravity. In the first case the fall of a fluid film positioned on the underside of a plate (the Rayleigh-Taylor flow) is studied. We show the results of simulation, which display the short-time rupture of the thin film, its break-up into "contracted" droplets, break-up of spikes and formation of bubbles. We have employed two discrete-particle techniques, molecular dynamics (MD) and dissipative particle dynamics (DPD) for thin-film flowing down a vertical wall. Two-dimensional models are constructed by assuming that the contact line dynamics control the thin-film flow. The flow patterns obtained are realistic in appearance and are in qualitative agreement with experimental and theoretical results. We have also unveiled the formation of fingering instability, rivulets and have observed horseshoe patterns.

Keywords: Coating flows; falling film flow; dissipative particle dynamics; discrete particle schemes; computer simulations

*Corresponding author.

1. INTRODUCTION

Fluid flow with a thin layer over a solid surface is of considerable technological and scientific importance. Many industrial processes, ranging from spin coating of microchips, fast drying paint production, to the design of photographic films, are based on thin-film dynamics. One encounters such film flows also in everyday life. Rain running down a windowpane, water dripping from a ceiling and the evolution of drying paint layers are typical examples of vertical thin-film flow. These many areas of application have stimulated the study of controllable thin-film dynamics [15, 16, 26, 31, 37]. Currently, this is a ongoing subject with growing research activity [49]. This field embraces experimental [5, 22, 30], theoretical [5, 6, 30, 32] and numerical [11, 23, 28, 48] studies.

When the films are subjected to the action of various mechanical, thermal or structural factors, they display interesting dynamical phenomena, such as wave propagation, wave steeping, fingering and the development of chaotic behavior. The force driving the coating flow is usually gravity and/or an externally applied pressure. One boundary surface of the liquid layer is its interface with the supporting fluid, the other fluid interface. If the ambient fluid is a dynamically passive gas, the film has a free surface as it flows down inclined planes. Coating flows are free-surface flows and as such are difficult be solved mathematically. The free surface is an integral part of the solution. In the solution scheme it must be guessed and this guess must be iterated upon until it satisfies the flow and free surface conditions at all points. Such films can display additional rupture phenomena; creation of holes, spreading of fronts and the development of fingers. In principle, the film dynamics is governed by the set of Navier-Stokes (NS) partial differential equations (PDE) supplemented by appropriate, moving boundary conditions. However, a full NS problem in extended spatial and time domains is difficult to solve, even with the most powerful modern computers. Therefore, a simpler, solvable description of the evolution, which is a sufficiently good approximation to the corresponding solution of the NS problem, is usually considered. The most popular case of such a simplification is known as the long-wave theory [37] – in which the problem is reduced to a single PDE, which describes the evolution of the film thickness in one spatial variable.

Lubrication equation is commonly used to describe thin-film or liquid layer dynamics, driven by the large surface tension [31]. A simplified

evolution equation (EE) is represented by the fourth-order non-linear PDE:

$$\frac{\partial h}{\partial t} + \nabla \cdot \left[\frac{h^3}{3} C \nabla \nabla^2 h + \mathbf{f}(h, \nabla h) \right] = 0 \tag{1}$$

where: $h(x, y, z, t)$ – is the fluid film thickness, C – the inverse capillary number (the ratio of surface tension to viscous forces) and $f(\cdot)$ is a non-linear function including the van der Wals forces and Marangoni effects. Apart from the simplest, particular and low dimensional cases [37] the Eq. (1), cannot in practice be solved analytically. Nevertheless, theoretical results based on perturbation methods in the evolution equation analysis (*e.g.*, long-wave, single-parameter and multiple-parameter approaches [15, 16]) produces many interesting results. They illustrate the principles of fluid film flows and allow for the assessment of the validity of the boundary conditions. According to theoretical considerations [15], a film thickness EE, which would provide a good-time-uniform approximation to large-amplitude waves on films flowing down vertical planes, does not exist. The EE solution exhibits steepening of the wavefronts, leading to wave-breaking in a finite time. A system of at least two coupled PDEs is needed for a good approximation of the long-wave regimes. However, the difficulty faced in attempting to solve them is correspondingly severe and can approach the level of difficulty in the original NS system.

In the last twenty years, computer power and progress in numerical methods have overcome some of the difficulties associated with free surface problems, which are now routinely solved by commercial packages. A package of this kind is NEKTON, which is designed specifically for coating flows [34]. More serious than free surface problems are the limits of validity of the approximate theories. As shown in [14], they may not be valid globally for all time, as it is in the case of large-amplitude regime for the evolution equation. Moreover, because of the problems with varying grid size in different dimensions, and the appearance of nearly singular solutions, which describe moving contact lines and film rupture, numerical computations are still delicate due to the tendency of the scheme to change sign and destabilize, when they are under-resolved in view of the fine scales developed [48].

We propose here an entirely different numerical model of fluid film dynamics from those, which can be derived from the NS approach or its asymptotic expansions. The model is based on the particle approach [10, 13,

21, 25, 45, 46] and can be used for simulating thin-film dynamics in the mesoscale. Instead of changes of film thickness in nodal points in time according to the evolution equation discretized in both space and time, the temporal evolution of particle system is governed by Newtonian laws of motion. Particles represent the "lumps of fluid", which interact each other *via* a two-body potential. In the first section of the paper the particle model is briefly described, focusing the attention on dissipative particle dynamics (DPD). Some results of DPD simulation of a liquid film lying on the underside of a horizontal plane and subject to the Rayleigh-Taylor instability are presented. Then we present the application of molecular dynamics and DPD in simulation of a sheet falling down a vertical wall. In the following sections we propose a numerical model based on the contact line dynamics and we present the results of these particle simulations. Finally the conclusions are summarized.

2. MD AND DISSIPATIVE PARTICLE DYNAMICS

Until recently, the numerical models of material, which are based on temporal evolution of ensemble of particles, have been used only in the micro-scale simulations with length scales up to 100 nanometers. The particles stand for atoms or, at most, molecules of the medium considered. The broad spectrum of molecular dynamics (MD) techniques [3, 19, 40] has been using for many years in studying of microscopic properties of fluids and solids. These properties can be computed by averaging of the statistical functions of particle positions and velocities as well as by computing the correlation functions and higher moments in length and time scales of nanometers and nanoseconds. The accuracy of such computations depends mainly on the number of particles in the statistical ensemble, *i.e.*, how many particles are simulated and how many timesteps performed. The increase of computer power in the last decade allows one to simulate by using MD techniques, millions of atoms in million of timesteps [4, 14, 20, 29, 33, 40, 43]. This opens up not only the possibility for numerical simulation of more and more complicated substances, *e.g.*, hydrocarbons, magmas, polymers, proteins, DNA *etc.*, but also enable the study on micro-hydrodynamical phenomena and other physical phenomena occurring on the border between the micro- and macro-worlds.

The pioneering works by Abraham [14], Rapaport [39, 40], Vashishta [33, 43] and others [1, 7, 18, 20, 24, 29, 41], show that MD can be used for investigations of statistical properties of particle ensemble in thermodynamic

equilibrium. Relatively large number of MD particles (*i.e.*, 10^6) under external stress, velocity or force field, temperature gradient or pressure can reveal very interesting collective behavior. It appeared, for example, that basic types of hydrodynamic instabilities (*i.e.*, the Rayleigh-Taylor, Rayleigh-Bénard, Richtmyer-Meshkov, Kelvin-Helmholtz instabilities) can occur also in the microscale [1, 29, 40]. The particle fluid flows in the presence of obstacle [39], penetration mechanism [8] and crack formation phenomena [20] can also be simulated, by using the same MD technique. Although the physical properties of granular field are different from those in the bulk and they change relatively fast increasing number of particles (*e.g.*, solid-liquid coexistence is observed over the range of temperature different than that for large systems [24]) its behavior in the microscale is qualitatively similar to that observed in the macroscale.

The implementation of MD in granular mechanics [18, 41] and flexible surfaces modeling [7, 44], where:

1. the particles are clusters of atoms,
2. interparticle potential between clusters is extracted from experimental data and theory,

shows that the scope of particle paradigm can be extended over a broader front. The above examples suggest that due to the changes in particle and interparticle potential definitions, this can also be applied as a simulation technique in the meso- and macroscale, going up to the micron-scale and beyond. Assuming that:

1. a particle is a "lump of fluid",
2. fluid consists of interacting particles with 2-body potentials,
3. interactions between particles define the physical properties of the particle system,
4. particle system may undergo the external interactions as: gravity, velocity fields, pressure or thermal gradients,
5. temporal evolution of particle ensemble obeys the Newtonian laws of motion,

we can formulate the fluid particle model (FPM) [13].

The FPM introduced by Español [12, 13], may be viewed as a Lagrangian discretization of the equations of isothermal fluctuating hydrodynamics. This represents a generalization of the smoothed particle dynamics (SPH) approach [25]. As shown in [13], at zero temperature and with no angular variables, the form of the FPM equations is identical to the form of the equations obtained in a simple version of SPH as applied to fluid system.

FPM is devised for simulating physical phenomena over wide spatial and time scales.

The particle models are not only restricted to the microscale and the mesoscale. In [45, 46], a general approach to the construction of macroscopic particle models was presented. The equations of motion for the particles can be derived directly from the partial differential equations of fluid mechanics. The macroscale particle model (SPH, for example) applied together with FPM and MD can be used in, so called, cross-scale simulations [10, 47], which combine three-hierarchical-stage particle models covering micro- and macro-properties of the system.

Within our present scope, we will focus our attention on a special case of FPM, namely, dissipative particle dynamics (DPD) model [2, 21, 27, 35, 36, 38], which was a precursor of the more generalized FPM paradigm [13]. DPD model has been investigating theoretically for past a few years, and represents currently a mature numerical method [50]. Let us assume that a system of *mesoscopic* particles can interact *via* direct conservative two-body potentials, as in molecular dynamics simulations but, moreover, the particles exert friction and Brownian forces on each other. The form of collision operator assumed in [36] takes the following form:

$$\Omega_{ij}^{n}(r_{ij}^{n}, \vec{\mathbf{p}}_{ij}^{n}) = \left[\alpha_{ij} - \gamma\omega_{ij}^{n}(\vec{\mathbf{e}}_{ij}^{n} \bullet \vec{\mathbf{p}}_{ij}^{n}) + \frac{\sigma\theta_{ij}}{\sqrt{\Delta t}}\right]\omega_{ij}^{n}$$
$$\omega_{ij}^{n} = 1 - \frac{r_{ij}^{n}}{R_{\text{cut}}} \tag{2}$$

where: R_{cut} – cut off radius; $\theta_{ij}, \alpha_{ij}, \gamma_{ij}, \sigma$ – DPD potential parameters [36], θ_{ij} – a random number from $[-1, 1]$ interval; $\vec{\mathbf{p}}_{ij}$ – difference between momenta of particle i and j, n – timestep number, i – particle index. The collision operator for the three types of particle models is of short-ranged nature, *i.e.*, for $r_{ij} > R_{\text{cut}}\,\Omega_{ij} = 0$. Due to the non-central character of the DPD operators, the total angular momentum is not conserved. The FPM model conserves total angular momentum due to the inclusion of a spin variable. Hence, the additional equation of angular momentum conservation in the Newtonian laws of motion should be included. However, for the 2-D DPD systems, violation of the angular momentum is not a serious problem. The dissipative and random interactions are chosen in such a way that the center of mass motion of each interacting pair is insensitive to their collective motion. In this way the system relaxes to equilibrium much faster than in MD simulations and, at the same time, the interaction conserves the total momentum. The second feature allows the system to exhibit hydro-

dynamic behavior from a macroscopic point of view. Unlike the inherently anisotropic lattice gas models [42], the particle model is isotropic and Galilean-invariant, and has the potential to be computationally efficient.

The temporal evolution of particles in the presence of gravitational and friction forces is described by the Newtonian momentum equations, which can be represented in the following discrete form:

$$\begin{aligned} \Delta\vec{\mathbf{p}}_i &= \sum_{i\neq j}(\Omega_{ij}\vec{\mathbf{e}}_{ij} + m_i g \cdot \vec{\mathbf{e}}_y - \lambda_i \vec{\mathbf{p}}_i)\cdot \Delta t \\ \Delta\vec{\mathbf{r}}_i &= \frac{\Delta t}{m_i}(\vec{\mathbf{p}}_i + \Delta\vec{\mathbf{p}}_i) \\ r_{ij} &= |\vec{\mathbf{r}}_i - \vec{\mathbf{r}}_j| \end{aligned} \tag{3}$$

where: $\Delta r_i, \Delta\vec{\mathbf{p}}_i$ – are the changes of position and momentum, respectively, for particle i of mass m_i, Δt – timestep, Ω_{ij} – collision operator, g – gravitational acceleration, λ – friction coefficient, $\vec{\mathbf{e}}_{ij}$ – unit vector pointing from particle j to particle i, r_{ij} – the distance between particles i and j. The type of the collision operator Ω_{ij} depends on the particle model used. For MD, Ω_{ij} can be represented, *e.g.*, by the Lennard-Jones potential, but for DPD model it is given by a two-body potential with a prescribed formula (2).

For the DPD particle model, we employ the second-order Adams-Bashforth (A-B) numerical scheme for integration of the Newtonian equations. In Figure 1, one can observe the fluctuation of kinetic energy of DPD particle system for $\sigma = 0$ (see Eq. (2)), which means that the kinetic energy should converge to zero for a dissipative system [36]. The application of A-B scheme is a reasonable compromise between the low-order inaccurate schemes used previously and the less efficient but self-consistent, higher-order schemes [37].

As shown in [27], one can assess the conditions and timescale DPD fluid describes an isothermal fluid kicked out of equilibrium. This was done on the basis of a non-linear kinetic equation – such as the Fokker-Planck-Boltzmann (FPB) equation – for the single particle distribution function. By solving the FPB equation, solutions to the Navier-Stokes equations can be obtained in the continuous limit. Therefore, DPD fluid can be treated as a fluid with granular properties, thus the DPD particle model fits well for simulation of very thin films in the mesoscale, where sample size is tens of micrometers and time-scale is of a few microseconds. Such a simulation with MD would take at least several years for 10^7 particles. Unlike the evolution

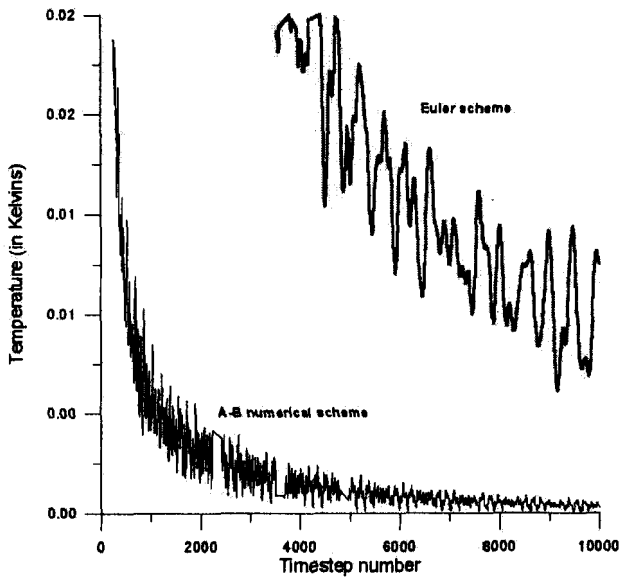

FIGURE 1 The fluctuation in the kinetic energy for the Euler (1st order) and Adams-Bashforth (2nd order) numerical schemes. For the higher-order scheme the 0 kinetic energy is approximated much better than for the lower-order method (note that the timestep $\Delta t = 1$ is in dimensionless units for DPD scheme, see [36]).

equation (EE), which is only an approximation to the NS equations and works in the macroscale, the DPD particle model represents a complete model of the mesoscale fluid. In this paper, its isothermal version is exploited, although dissipative particle dynamics is also feasible [2] with energy conservation, which can sustain temperature gradients and heat flow. In a sense, DPD is a mesoscale approximation of the microscopic MD paradigm, and, if necessary, DPD can be combined together with MD in cross-scale simulations [10, 14], where the MD model is applied simultaneously to phenomena occurring in time and length scales close to the DPD resolution.

3. RAYLEIGH-TAYLOR DYNAMICS IN THIN FILM

We consider a simple case of thin-film dynamics, *i.e.*, in which gravity is present and surface tension is constant and the layer is thin. When a film is positioned on the underside of a plate, the Rayleigh-Taylor instability flow can be observed (see Fig. 2). For theoretical analysis, a simplified version of

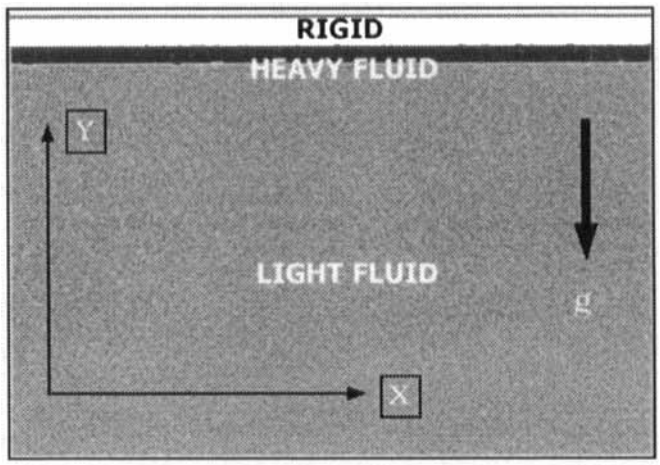

FIGURE 2 Initial conditions of DPD simulation of a thin liquid film on the underside of a rigid plane.

evolutionary equation (Eq. (1)) is used [37]. However, for very thin films, molecular forces and surface tension varying with fluid thickness should also be taken into account. Therefore, for investigating its long time evolution including droplet detachment and its fragmentation, the EE approximation may be insufficient.

For this reason, we have applied the DPD model for computer simulation of this phenomenon, instead of the Navier-Stokes equations. Let us assume that both fluids are made of DPD particles. The initial situation is depicted in Figure 2. The plane is also covered with particles, but we assume that they are motionless and reflective. DPD model parameters are provided in Table I. They are similar to the values presented in [36], except m_i and γ_i, which values are different for both fluids. A large body of a lighter fluid overlies a thin liquid film on the underside of a rigid plane. Particles are confined in the computational box with periodic boundary conditions, however, due to the rigid plane, the particles can move freely only in x direction. For fewer particles the influences of boundary conditions become evident. The thin-film fluctuations develop feedback tendencies and produce artificial disturbances. Moreover, the instabilities, occurring in the ambient (lighter) fluid, do not dissipate away. Additionally, smaller particles ensembles generate artificial, numerical fluctuations, which cannot be quickly dissipated. For about 10^5 DPD particles, both the numerical fluctuations and influences produced by the boundary conditions can be safely neglected.

TABLE I The DPD model parameters for two immiscible fluids (in dimensionless units, see Eqs. (2–3) and [36])

Model Parameters	*Heavy fluid* (1)		*Light fluid* (2)
α	7.063		7.063
$\alpha_{1,2}$		7.487	
γ	5.650		0.565
$\gamma_{1,2}$		0.565	
λ		0	
σ		1.290	
g		10	
m	1		0.1
Δt		0.1–1	
N (number of DPD particles)	20,000		100,000
R_{cut}	1.3		1.3
L_x (box size)		180	
L_y (box size)		180	
Integration time		3,000–70,000 timesteps	

A difficult problem in DPD is the fitting of the collision operator parameters (see Eq. (2)) to the time and length scale under consideration. Because there is not experimental methods, which can directly measure these values, they can be obtained only by matching macroscopic parameters such as temperature, pressure, surface tension, viscosity *via* formulae taken from non-equilibrium statistical mechanics to the DPD model parameters. This process is difficult and involves many iterations, *e.g.*, by using Schwarz iterative procedure [51]. A very interesting algorithm is proposed in [13]. It is based on the Voronoi tesselation scheme, and allows one to assess collision operator parameters for DPD particles in a direct way. However, studies concerning matching between particle approach in mesoscale and macroscale fluid properties are still in a stage of infancy. In the papers [21, 35, 36], which deal with the phase separation in two-dimensional binary immiscible fluids, the DPD collision operator parameters for the fluids investigated, the size of computational box and the time-step are given in dimensionless units (see Tab. I). We use similar values as in [36] due to the lack of any other physical information. The simulation time is given in timesteps Δt, where we have set $\Delta t = 1$ in dimensionless units used in [35, 36].

In Figure 3 we show a few snapshots of two-dimensional DPD simulation of falling film. Because of initial interfacial disturbances caused by the particle motion and the Brownian factor in DPD collision operator (see Eq. (2)), the fluid-fluid interface becomes unstable and fingering instability can be discerned. During the evolution of the particle system shown in Figure 3, we observe the following processes:

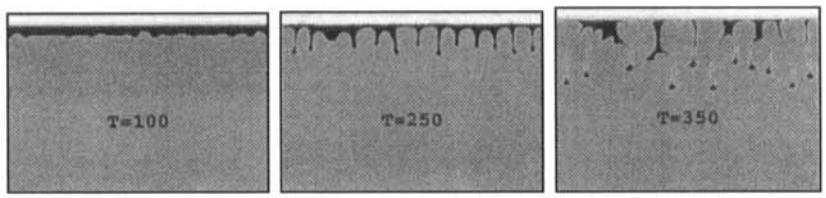

FIGURE 3 A few snapshots from DPD simulation of a thin liquid film falling down from the underside of a rigid plane (a Rayleigh-Taylor type of flow). Time is given by the number of timesteps (timestep $\Delta t = 1$).

1. the film rupture, *i.e.*, at a certain location the local thickness of the film becomes zero (see Fig. 4),
2. droplet detachment (see Figs. 3 and 5),
3. droplet fragmentation (see Fig. 6),
4. breaking-up of spikes (see Fig. 7),
5. development of complicated mixing patterns (see Fig. 8).

The mechanisms of thin-film rupture, droplet detachment and its fragmentation have already been investigated by many authors (see review papers [31, 37], for example). When the film becomes very thin, in the range from 100 to 1000 Å, the film thinning process becomes faster and for a critical thickness we observe clearly the rapid break-up caused by the molecular forces. Because we have assumed that the rigid plane is reflective (the film cannot adhere to the surface), the film fragments form spherical droplets after breaking-up. This process is displayed in Figure 4. The droplet detachment (see Fig. 5) occurs before the breaking-up of the spikes, which can also produce small droplets as these depicted in Figure 4. As shown in Figure 7, large droplet can be fragmented into two smaller ones in the similar way as in the physical experiment described in [17]. Unlike miscible fluids [17], in the

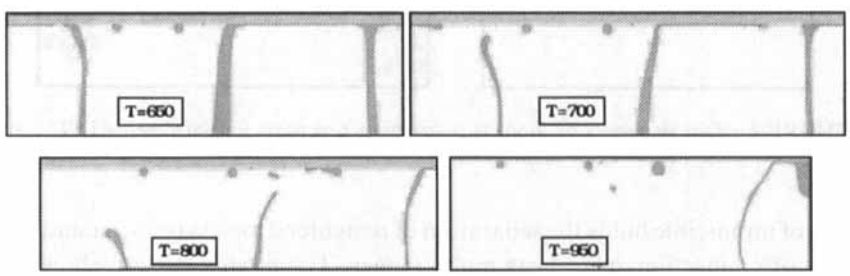

FIGURE 4 The sequence of snapshots from DPD simulation representing rapture of the thin film and droplets formation. Time is given by the number of timesteps (timestep $\Delta t = 0.5$).

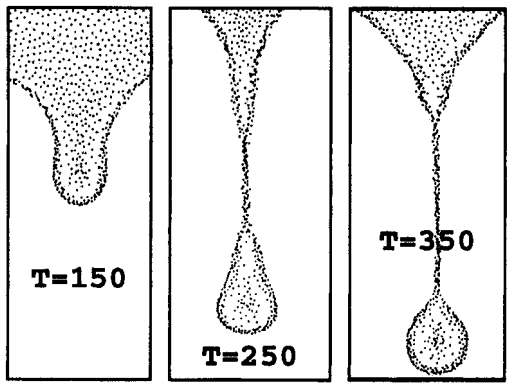

FIGURE 5 Droplets detachment process. The picture show the creation of a very small droplet, which consists of about a hundred of DPD particles. One hundred DPD particles are concentrated at the juncture of the necking process. Time is given by the number of timesteps (timestep $\Delta t = 0.5$).

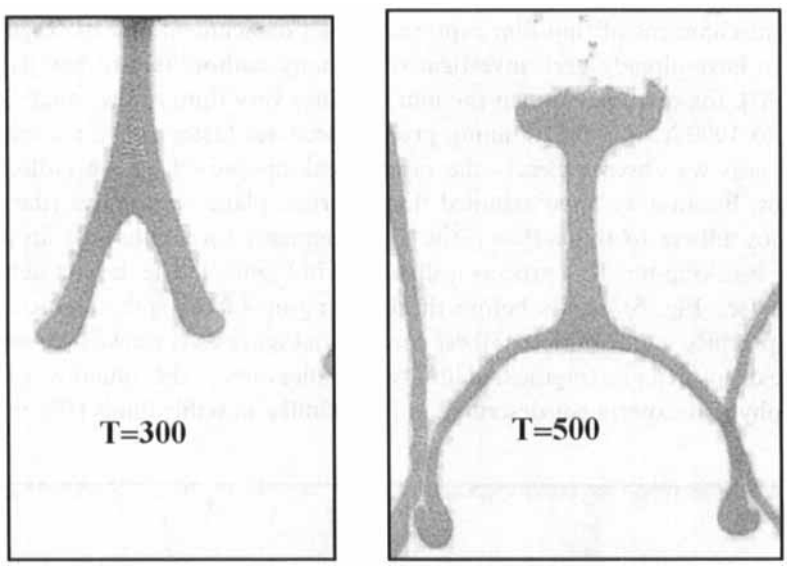

FIGURE 6 Two snapshots of droplets fragmentation process simulated using DPD code. Time is given by the number of timesteps (timestep $\Delta t = 1$).

case of immiscible fluids the separation of daughter droplets is slower and life-time of connection spike lasts much longer. The mixing pattern shown in Figure 8, obtained by using the DPD model, consists of very small droplets, long spikes and large shapeless structures.

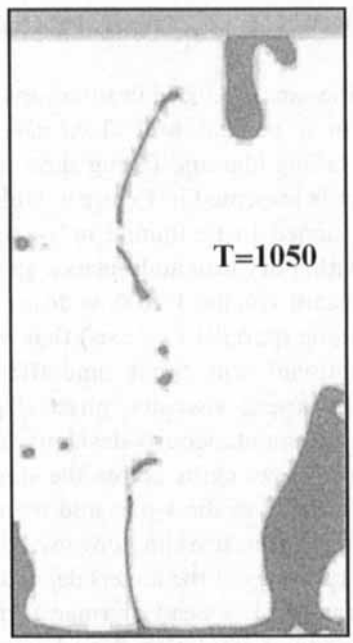

FIGURE 7 Break-up of spikes in the Rayleigh-Taylor thin film flow simulated using DPD code. Time is given by the number of timesteps (timestep $\Delta t = 0.5$). This frame comes from the same simulation in Figure 4.

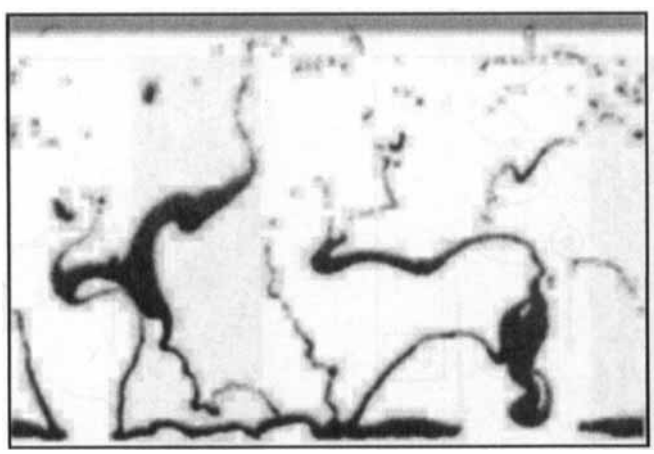

FIGURE 8 A snapshot of DPD simulation of a thin liquid film falling down from the underside of a rigid plane. Complicated mixing pattern can be observed. This frame comes from the same simulation in Figure 3, $T = 1100 \times \Delta t\,(\Delta t = 1)$.

4. FILM FALLING DOWN A VERTICAL PLANE

Other types of instabilities are produced in situations with a thin film falling down inclined plane or a vertical wall. Two cases of such a flow are considered separately: falling film and falling sheet problems [26, 37]. The difference between them is presented in Figure 9. Unlike the first case, when film falling down is assumed to be infinite in x-axis direction, for falling sheet case one begins with a dry wall and opens a gate at $x = 0$. This allows the viscous fluid of constant volume V to flow down the wall (along x-axis) with a straight contact line (parallel to z-axis) that moves according to the direction of the gravitational field. Some time after the release (the time depends on the fluid thickness, viscosity, physical properties of the wall surface *etc.*), a contact line spontaneously develops and produces a series of fingers of fairly constant wavelengths across the slope. Either long fingers develop with the sides parallel to the x-axis and with the roots fixed to the plate, or triangular fingers form, traveling downward with their roots moving downward. The morphology of the fingers depends on the contact angle. As the sheet moves downward, a bead or ridge forms behind the leading edge. This is formed due to recirculation flow down along the free surface toward the contact line and returning along the plate. This flow is caused by the presence of the contact line, which slows down the film drainage. High pressure near the contact line is responsible for ridge production. As shown in [31, 37], there exist two theories which produce similar ridges by assuming the existence of: (1) the contact line and (2) precursor layer and no contact

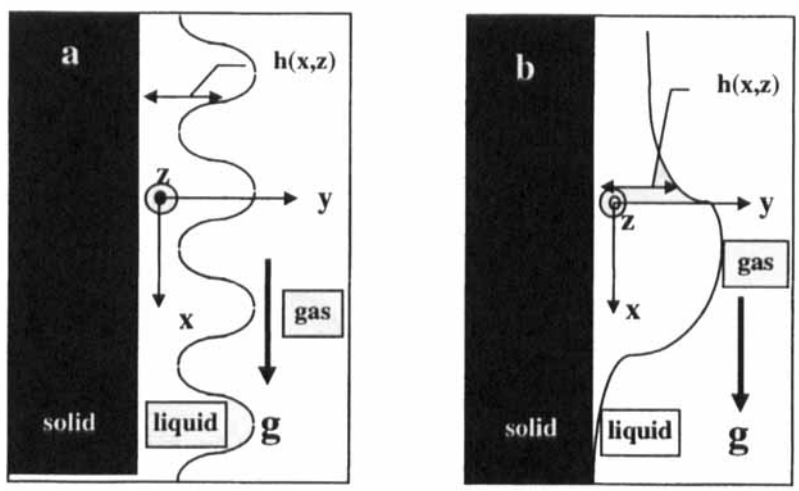

FIGURE 9 Thin liquid film (a) and liquid sheet (b) falling down a vertical wall.

line. Unlike the inclined plane, where the tilt angle decides the ridge existence, it is always present in vertical wall case. According to theory and experiments [37], a perturbed capillary ridge has thicker regions of liquid advancing more rapidly than the thinner regions.

In [22], one finds a discussion of the "double role" of contact-line resistance in contact-line and fingering dynamics of macroscopic spinning drops and gravity-driven films. The larger resistance at the wedge segments of the finger head or during flow initiation results in larger liquid accumulation and, consequently, increases the subsequent rate of spreading. This also results in an increase in the ridge thickness, detected in the gravity-driven fingering experiments. In the case of complete wetting, intermolecular forces, comparable to the main driving force, are powerful enough to exceed viscous dissipation in a wedge and, hence, overcome this accelerating effect. Thus, the contact line not only increases the resistance to the flow, but also provides an appreciable driving force on the fronts of the falling film.

From this scenario, we propose a new 2-D numerical particle model of falling sheet evolution [47], which can be considered as a supplementary one to the EE theory. Let us consider two particle systems as shown in Figure 10. For the first system the 1.2×10^5 particles are initially placed in the black region of

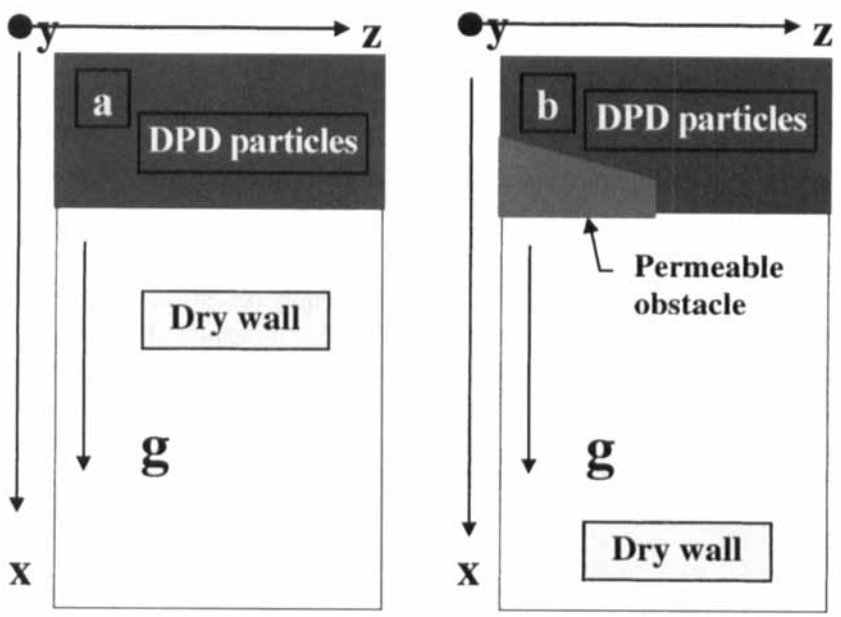

FIGURE 10 Two particles systems simulated. The number of DPD particles (a) 1.2×10^5 (b) 1×10^5 – fluid, 3×10^4 – obstacle.

computational box. This region stands for a vertical wall covered by the particle fluid. The white part of the box represents dry wall. In the second system (Fig. 10b), the motionless obstacle is added. It consists of about 3×10^4 particles and depending on their spacing and interparticle potential assumed, the obstacle can be both impermeable or permeable. Periodic and reflecting boundary conditions are assumed in z and x directions, respectively. There is not additional supply of fluid to the system. Unlike the R-T case and the situation shown in Figure 9, a x-z coordinate system is considered. The y dimension axis, which follows the fluid thickness, can be neglected, assuming that:

1. Fluid film is very thin. Therefore, there is a constraint on the distance between two particles $R_{ij}(x, y, z) \approx r_{ij}(x, 0, z)$ and $\Omega(R_{ij}) \approx \Omega(r_{ij})$ for $r_{ij} > h$ (where h is the fluid thickness).
2. Interactions between particles are soft, *e.g.*, for simulating a few particle layers placed one upon another, constant repelling force should be considered for $r_{ij}(x, 0, z) < \sigma$, then the approximation assumed above will be valid also for small r_{ij}.
3. The observed particle density represents a projection of the "real particle density" on x-z plane, therefore the large and small film thickness can be reflected by both high and low particle densities, respectively.

These theoretical results can be summarized as:

(A) a ridge forms behind the leading edge,
(B) the ridge has thicker regions of liquid advancing more rapidly than the thinner regions,
(C) the contact-line resistance plays a "double role" not only in slowing-down but also by increasing the rate of spreading.

Let us assume furthermore that a particle i undergoes large friction force, when the number of particles *Neigh*(i) in its vicinity (in cut-off radius sphere, see Eq. (2)) is too small, *i.e.*, when *Neigh*(i) < *Neighmin*. This particular procedure in the DPD algorithm is shown below:

$$Damphi = \frac{\lambda \Delta t}{2}$$

if(Neigh(i) < Neighmin)

$Damphi \approx 1$

else

$Damphi = small$

endif

$$\mathbf{p}_i^{n+1/2} = \frac{(1 - Damphi)}{1 + Damphi}\mathbf{p}_i^{n-1/2} + \frac{\Delta t}{1 + Damphi}\left(\sum_{j \in R_{\text{cut}}} \Omega_{ij}^n + m_i g \bullet \vec{\mathbf{e}}_Y\right) \tag{4}$$

The last equation in (4) represents the discretized and transformed Newtonian equation of motion (see Eqs. (3))

The first model was constructed by assuming that the particles interact *via* a two-body conservative Lennard-Jones (LJ) potential. To be consistent with the assumptions (1) and (2), the potential is truncated (see Eq. (5) and Fig. 11). Therefore, this potential is softer (less steep potential) in comparison to the original one, and consequently allows the particles to coalesce in lobes and ridges.

$$\Omega_{ij}^n = \begin{cases} \dfrac{24\varepsilon}{R_{\text{soft}}}\left[\left(\dfrac{\sigma}{R_{\text{soft}}}\right)^6 - 2\left(\dfrac{\sigma}{R_{\text{soft}}}\right)^{12}\right] \cdot \vec{\mathbf{e}} & \text{for } R_{\text{soft}} > r \\ \dfrac{24\varepsilon}{r}\left[\left(\dfrac{\sigma}{r}\right)^6 - 2\left(\dfrac{\sigma}{r}\right)^{12}\right] \cdot \vec{\mathbf{e}} & \text{for } R_{\text{soft}} < r < R_{\text{cut}} \\ \vec{\mathbf{0}} & \text{for } r > R_{\text{cut}} \end{cases} \tag{5}$$

Examples of these results are presented in Figures 12, 13. In the first figure one can observe the triangular fingers, traveling downward with their roots moving downward as well. The finger-shaped contact-line establishes very fast. The triangle-shaped obstacle, placed in the middle of the flow, produces the avalanches – rivulets – falling down prewetting surface of the

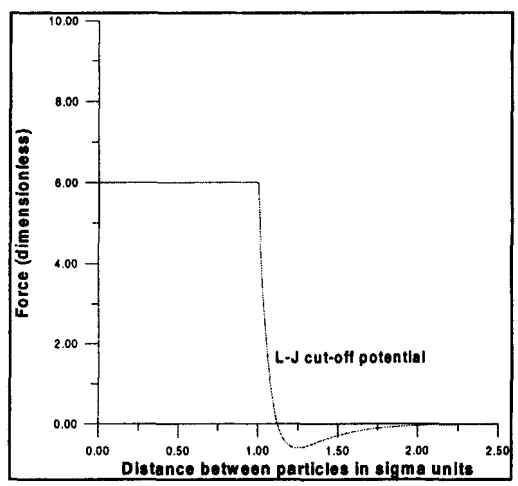

FIGURE 11 Truncated L-J potential. The values are given in dimensionless units [36].

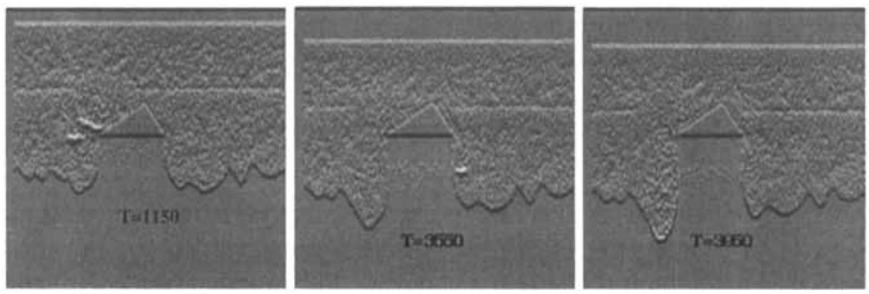

FIGURE 12 A few snapshots of MD simulation of falling film in presence of triangular obstacle. Initial planar particle density is equal to 20 (in dimensionless units) and **Neighmin** = 20 particles. Time T is given by the number of timesteps ($\Delta t = 0.1$). 10^5 MD particles are simulated.

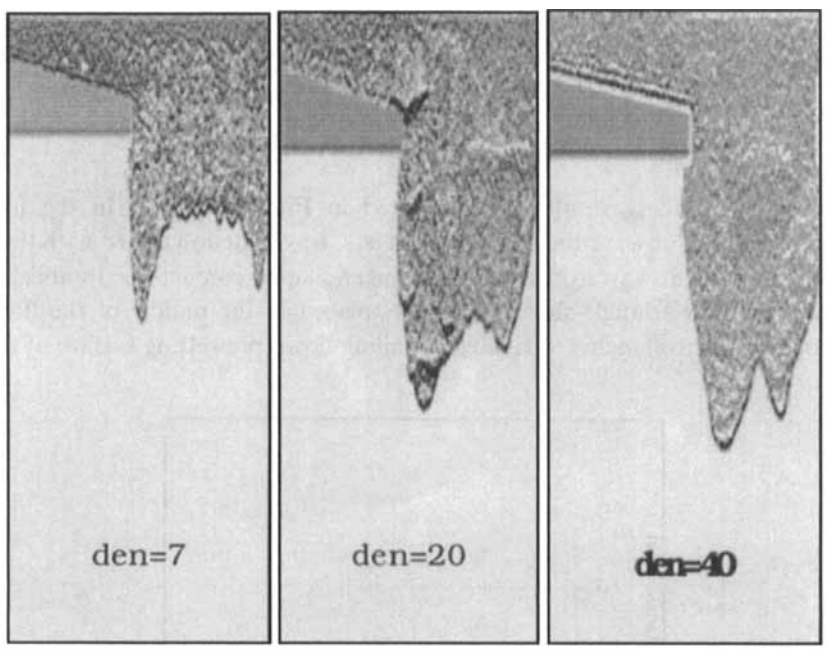

FIGURE 13 MD simulation results of falling film for various initial particle densities (**Neighmin** = 13, 20, 30, particles respectively). Time $T = 4000 \times \Delta t$ ($\Delta t = 0.1$). 10^5 MD particles are simulated.

wall. The rivulets appear spontaneously close to the triangle sides. As shown in Figure 12, most of them lie close to the side with a lower inclination, *i.e.*, the flow resistance higher. The longest finger is close to the more inclined triangle side. A similar situation can be seen in Figure 13. For increasing the

density, the gap between triangle-shaped "fingers", which can be seen for both sides of the obstacle, zoom-ins and eventually the V-shaped single "finger" appears.

The Lennard-Jones potential is not suitable for modelling of fluid particle interaction in the mesoscale. The LJ particles are similar to the spherical granules (soft spheres) than to the viscous fluid particles. For this reason, we have employed the DPD, shear-dependent, collision operator (Eqs. (2)) in the following model. Simple critical condition applied in the MD model (see "*if*" statement in Eqs. (4)) is also insufficient and, in practice, limits the thin-film evolution to the contact line dynamics. By using results obtained for 3-D theoretical considerations and experiments, the "*if*" statement (see Eqs. (6)) should be strengthened by additional conditions, which simulate the third dimension not considered in the model. The second component in the "*if*" statement in (4) reflects the approved fact [37] that the fluid falling down an inclined plane is transferred literally into growing lobes at the expense of thinner part of the ridge. Therefore, the fluid behind the ridge is moving faster than that closer to its leading edge. The third "*if*" component allows one to assume that very thin film of particles can stick to the wall and moves very slowly. The section of the numerical procedure, which governs the DPD particle dynamics, is shown below.

$$
\begin{aligned}
&Damphi = \frac{\lambda \Delta t}{2} \\
&\textbf{if}(\textbf{Neigh(i)} < \textbf{Neighmin} \;\&\&\; \sum_{j \in R_{\text{cut}}} (\mathbf{e}_{ij}^n \bullet \tilde{\mathbf{p}}_{ij}^n) > 0 \| \textbf{Neigh(i)} < \textbf{Neighlow}) \\
&\quad Damphi \approx 1 \\
&\textbf{else} \\
&\quad Damphi = small \\
&\textbf{endif} \\
&\mathbf{p}_i^{n+1/2} = \frac{(1 - Damphi)}{1 + Damphi} \mathbf{p}_i^{n-1/2} + \frac{\Delta t}{1 + Damphi} \left(\sum_{j \in R_{\text{cut}}} \Omega_{ij}^n (r_{ij}^n, \tilde{\mathbf{p}}_{ij}^n) \right) \\
&\tilde{\mathbf{p}}_i^n = \frac{1}{2} (3\mathbf{p}_i^{n-1/2} - \mathbf{p}_i^{n-3/2}) \;\; \tilde{\mathbf{p}}_{ij}^n = \tilde{\mathbf{p}}_i^n - \tilde{\mathbf{p}}_j^n
\end{aligned}
\tag{6}
$$

In order to demonstrate this algorithm, we study the particle system shown in Figure 10a. Unlike the previous case, we are not interested in the contact-line dynamics, but rather in the evolution of expanding fluid. Let us compare the results of simulation shown in Figure 14 with the film falling down inclined plane (Fig. 9a) scenario [26]. According to this scenario,

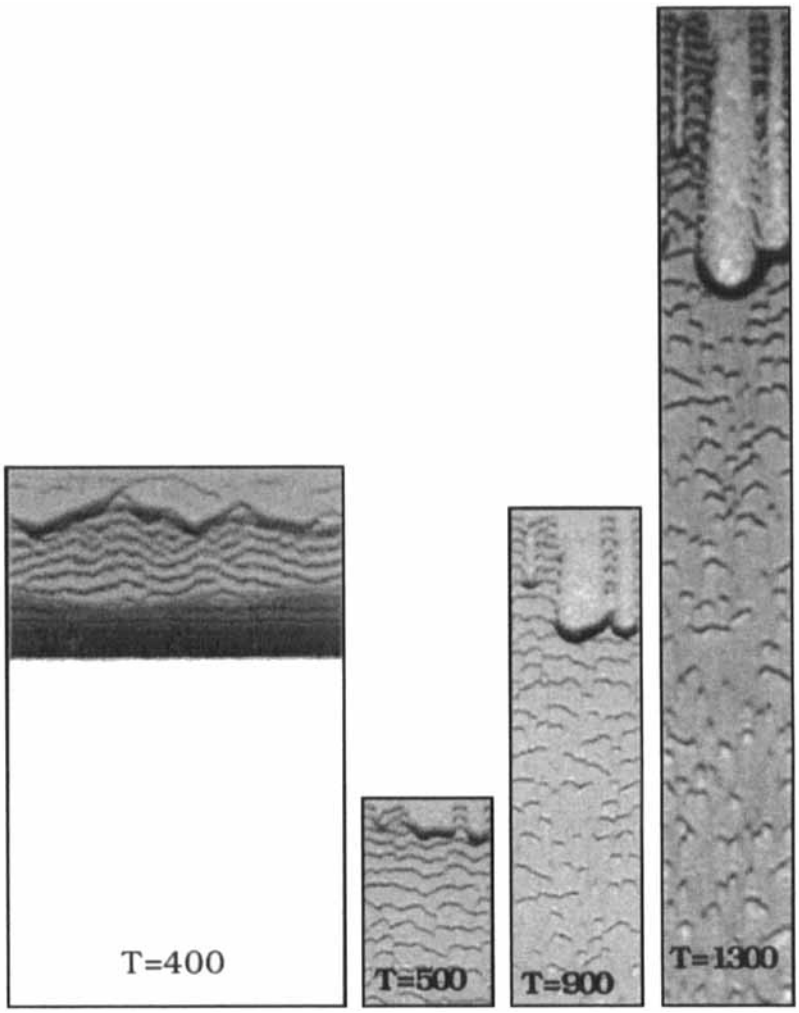

FIGURE 14 Falling sheet scenario, simulated using DPD model (2.0×10^5 particles are simulated). Time T is given by the number of timesteps ($\Delta t = 0.1$).

which entails

1. 2-D waves with straight wave fronts are excited first,
2. 3-D "synchronous" (*i.e.*, the neighboring wave fronts are in phase) or "asynchronous" patterns with transverse modulations appear,
3. wave-fronts begin to break (for the "synchronous" case), leading to disordered patterns or "herringbone" patterns to appear in patches (for the "asynchronous" case).

The "horseshoe" patterns for disordered flows can be observed for both "synchronous" and "asynchronous" flows. Strange attractors like V-shaped array of larger-amplitude bulges, which move in the "sea" of smaller-amplitude bumps subpatterns, appear for strongly dispersive case of flow [15, 16]. This scenario describes the temporal evolution of:

1. fluid film without contact-lines (leading edge and trailing end), *i.e.*, assuming constant supply of fluid on input ($x = 0$) and its removal on output ($x = L$),
2. constant – in average – fluid thickness,
3. small inclination angle of the plane,

the highly unstable fall of sheet down a vertical wall produces considerably different patterns. The difference occurs at the initial stages of the flow, when both leading edge and trailing end dynamics do not allow for creation of straight wave fronts. This "synchronous" instability can be observed (see Fig. 14, $T = 400 \times \Delta t$, where Δt is timestep). The wave fronts becomes large in amplitude and begin to break ($T = 500 \times \Delta t$). Subsequently, the flow becomes disordered ($T = 900 \times \Delta t$). The "horseshoe" patterns obtained ($T = 1300 \times \Delta t$) are similar to those presented in [15, 16]. Unlike the steady film flow case, the instability of the trailing end caused by the lack of fluid influx results in the production of both expanding avalanches and rivulets with their sides parallel to the x-axis (see Fig. 14).

We have obtained interesting results for the particle system shown in Figure 10b. Because of the "*if*" statements in Eqs. (6) and the extreme values of the parameter *Damphi* assumed, the simulated cases are strongly dispersive. The "double role" of contact-line resistance, reported in [22], is clearly visible. As shown in Figure 15, the V-shaped contact-line spreads very fast down a "dry" wall, due to larger liquid accumulation at the leading edge. The fingers, which appear later, are due to trailing end instability and rivulets created by the permeable obstacle. They are much slower than the V-shaped contact-line, despite they are falling down the "prewetted" wall. Such behavior comes from the intermolecular forces [22], which are comparable to the main driving force and seem to be powerful enough to exceed viscous dissipation in a ridge and hence overcome its accelerating tendency. Due to the amplification of the accumulation effect by increasing the value of *Neighmin*, the initial flow becomes faster. The quasi-stationar bulges appear on the V-shaped edge of fluid (see Fig. 16). As before, this structure is eventually destroyed by secondary fingers and rivulets.

The spontaneous emergence of avalanches, droplets and rivulets is very difficult to simulate with classical fluid dynamical models, due to the critical

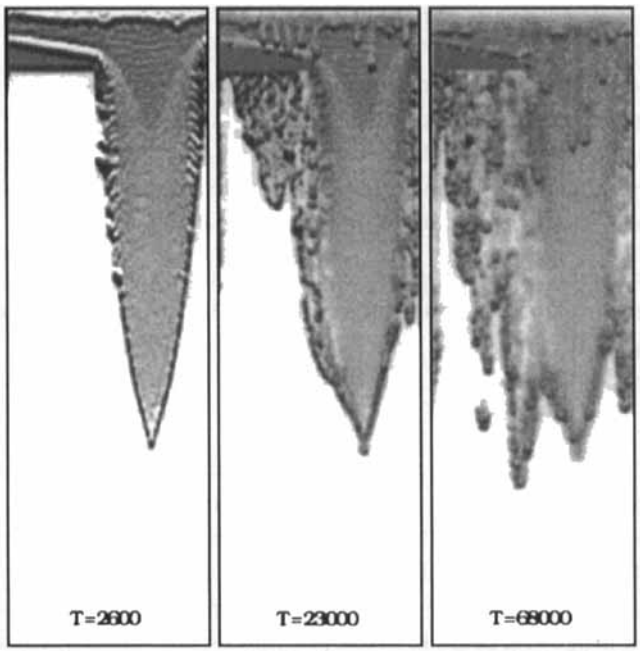

FIGURE 15 Snapshots from computer simulation of falling sheet by using DPD model. Initial density den = 20 ***Neighmin*** = 30. Time T is given by the number of timesteps ($\Delta t = 0.1$). 2.0×10^5 DPD particles are employed.

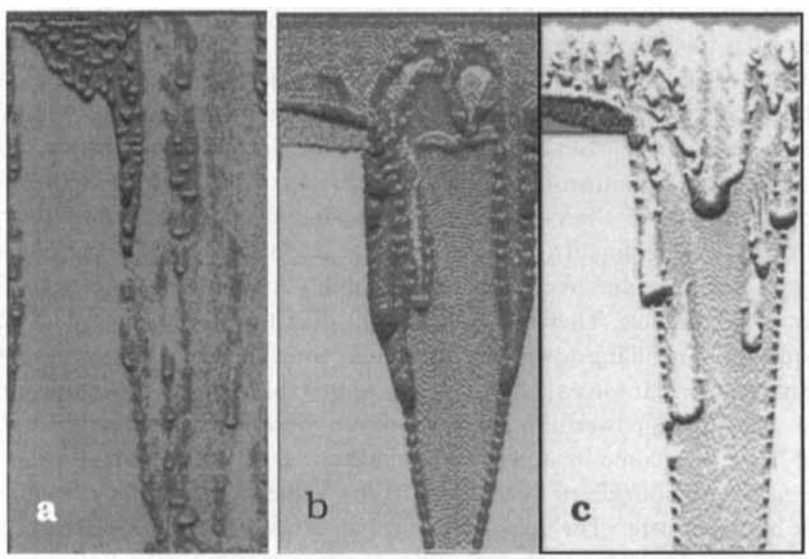

FIGURE 16 Snapshots from computer simulation of falling sheet by using DPD model. Initial density den = 20. (a) ***Neighmin*** = 40, $g = 1$ (b) ***Neighmin*** = 50, $g = 1$ (c) ***Neighmin*** = 50, $g = 2$ (gravitational acceleration **g** is given in dimensionless units). The simulation time is the same for the three snapshots, *i.e.*, $T = 800$ timesteps ($\Delta t = 0.1$). 1.2×10^5 DPD particles are employed.

nature (self-organized criticality) and threshold character of these nonlinear phenomena. Therefore, the role of statistical fluctuations in thin-film dynamics cannot be underestimated, especially in the mesoscale. Unlike the classical approaches, we need not introduce any external and artificial perturbations. All phenomena occur spontaneously due to thermal noise inherent in the nonlinearly interacting particle dynamics.

5. CONCLUDING REMARKS

In the paper we have proposed a novel numerical method for simulating coating flows. This technique is based on dissipative particle dynamics, and according to the assumptions of DPD formulated in [21, 27, 36] this technique can be applied for investigations of nano-scale thin-film flows. The particle model can be treated as complementary to the classical paradigms, which base on lubrication approximation and the evolutionary equation (1). The validity conditions and the macroscale character of the Navier-Stokes, shallow-water equations restrict the scope of application of these models. The level-set method [52] may help to bridge the gap between the continuum approach and the DPD technique.

The granular character of the particle fluid and high thermal fluctuations inherent in the definition of particle model makes it suitable for investigating phenomena occurring in the mesoscale. We show that the model can be used for simulating the Rayleigh-Taylor thin-film flow, which displays similar properties to those observed for the models based on the EE approximation. By using DPD model one can simulate the fingering type of instability, droplet detachment, break-up of spikes, droplet fragmentation and others. A two-dimensional DPD model is also proposed for sheet falling down a vertical plane. The third dimension is simulated by the critical conditions constructed on the basis of some theoretical considerations and results of laboratory experiments. Our results obtained here are encouraging and display many features observed in the real flows.

Unlike MD based numerical models used in micro-hydrodynamics [9, 29], the particle models presented are very efficient. The CPU time needed for simulation of 10^5 particles in 10^4 timesteps does not exceed a few hours on a workstation. The models presented can be relatively easily extended to the three dimensions. However, in 3-D situations, the number of particles representing ambient gaseous medium becomes very large, and we expect that the computational efficiency will decrease substantially. Therefore, in the

near future we would like to adapt an existing parallel 3-D MD code for our models needs. Moreover, we plan to extend our isothermal DPD models to the non-isothermal case [2] or replaced them by more general FPM model [12, 13]. As shown in [13], the scope of FPM application is much broader. It includes both isothermal SPH and DPD as particular cases. Thus both macro- and mesoscale thin-film dynamics can be simulated, using a single FPM particle model.

Some advantages of the particle model application in the simulation of thin-film dynamics can be summarized as follows:

1. the particle model is gridless, thus the problems with remeshing and mesh singularities do not exist for film rupture and droplets detachment,
2. the model is very simple and can be modified easily,
3. the complicated boundary conditions, *e.g.*, permeable obstacles, rough surfaces, free surface, surface with surfactants or with chemical reactions, can be easily simulated by using particles,
4. large-amplitude perturbations can be investigated and long-time film evolution observed,
5. particle model can be interpreted as a Lagrangian discretization of the non-linear fluctuating hydrodynamic equations. Thus it can be applied to nano-scale, thin-film dynamics, where thermal fluctuations cannot be neglected,
6. particle model can be applied to the cross-scale simulations in which the collision operator is changed, depending on the spatial and time scale of the process being studied [10].

A serious drawback of the particle model is our limited experience with its application to real-life technological problems where quantitative results are expected. The current difficulty with the particle model comes from the different scales of resolution in time and space of the overlapping regions. In the future multiresolution algorithms [33] may hold the key to achieving such extreme-scale applications.

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