Spreading Dynamics of Nanodrops: A Lattice Boltzmann Study

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Spreading of nano-droplets is an interesting and technologically relevant phenomenon where thermal fluctuations lead to unexpected deviations from well-known deterministic laws. Here, we apply the newly developed fluctuating non-ideal lattice Boltzmann method [Gross et al., J Stat Mech, P03030 (2011)] for the study of this issue. Confirming the predictions of Davidovich and coworkers [PRL 95, 244905 (2005)], we provide the first independent evidence for the existence of an asymptotic, self-similar noise-driven spreading regime in both two- and three-dimensional geometry. The cross over from the deterministic Tanner’s law, where the drop’s base radius $b$ grows (in 3D) with time as $b \sim t^{1/10}$ and the noise dominated regime where $b \sim t^{1/6}$ is also observed by tuning the strength of thermal noise.

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I. SPREADING OF NANO-DROPLETS

The spreading of a viscous liquid droplet on a solid substrate is a fundamental and long-studied phenomenon [1–3] of relevance to many applications, such as, for example, painting or coating techniques. If a small macroscopic droplet is placed on a perfectly wetting substrate, one expects that, after an initial transition period, the base radius (see Fig. 1) increases according to a power-law, $b(t) \propto t^n$, with an exponent $n = 1/10$ in 3D and $n = 1/7$ in 2D. This relation can be derived from lubrication theory [1, 4] and is known as Tanner’s law [5].

The experimentally observed value of the exponent $n$ often deviates from the theoretical predictions and is found to depend on several physical parameters, such as substrate roughness, liquid viscosity or vapor density. This is reflected in the range of values that have been reported by experiments [6] and simulations [7–9].

Most experiments deal with the spreading of droplets that are at least of micrometer size and thus are unaffected by thermal fluctuations. It is, however, interesting to ask what happens to droplets at the nanoscale, where thermal fluctuations become important. Recently, the spreading of droplets under the influence of thermal fluctuations has been investigated numerically and theoretically [10]. There, a stochastic lubrication equation of the form

\begin{equation}
\partial_t h = -\frac{\sigma}{3\eta} \nabla \cdot (h^3 \nabla \nabla^2 h) + \sqrt{\frac{2k_BT}{3\eta}} \nabla \cdot \left[ h^{3/2} \xi \right]
\end{equation}

has been proposed for the evolution of the film height $h$ of the spreading droplet (see also [12]). Here, $\sigma$ is the surface tension, $\eta$ the dynamic viscosity, and $\xi$ is a Gaussian white noise with unit variance,

\begin{equation}
\langle \xi(r,t)\xi(r',t') \rangle = \delta(r-r')\delta(t-t')
\end{equation}

Since the total volume $V$ of the droplet is conserved, one additionally requires

\begin{equation}
V = \int d\vec{r}h(\vec{r},t) = \text{const.}
\end{equation}

The lubrication equation (1), which is a fully nonlinear stochastic differential equation with multiplicative noise, can be derived from the Navier-Stokes equations for a liquid film amended with the usual Landau-Lifshitz random stress

\begin{figure}[h]
\centering
\includegraphics[width=0.3\textwidth]{fig1.pdf}
\caption{Geometry of a spreading droplet on a solid substrate. $h(\vec{r},t)$ is the local height, $b(t)$ the base diameter and $\vec{r}$ is the coordinate in the plane of the substrate.}
\end{figure}
tension is 0 along the surface energy, no averaging is necessary to improve the static accuracy and the plots are thus each obtained from a completely equivalent measure of the droplet size. Furthermore, since the noise intensities are weak compared to the size of the simulation domain is $L \times L = 1200 \times 110$, with periodic boundary conditions along the $x$- and solid wall boundary conditions along the $y$-axis. The interface width is approximately 5, the surface tension is 0.0027, the liquid and vapor densities are $\rho_L = 1.0$, $\rho_V = 0.1$ and the relaxation times are set to $\tau = 1.0$. It is found that, in the present case, both the base radius $b(t)$ and the variance of the height profile, $s(t)$ [eq. (5)], give a completely equivalent measure of the droplet size. Furthermore, since the noise intensities are weak compared to the surface energy, no averaging is necessary to improve the static accuracy and the plots are thus each obtained from a single simulation. Owing to the slowness of the spreading process, the data had to be acquired over more than $10^7$ timesteps. For the present setup, the conditions of eq. (6) predict that noise dominates when $h/h_0 \lesssim 0.1$, in good agreement with our simulations.
spreading dynamics of nanodrops on perfectly flat solid surfaces. So far, Molecular Dynamics studies could not reach the literature, it seems to be not completely clear what precisely the effect of the vapor viscosity is on spreading.

In this work the newly developed fluctuating non-ideal fluid LB model has been applied to the study of the spreading dynamics of nanodrops on perfectly flat solid surfaces. So far, Molecular Dynamics studies could not reach...
FIG. 3: Instantaneous droplet profiles in the self-similar spreading regime in 2D, (a) without and (b) with noise. The insets show the rescaled droplet profiles (the rescaled height $h(t)|r|$ is normalized to one). Simulation parameters are as in Fig. 2a.

the asymptotic, self-similar spreading regime. Our simulations provide the first independent evidence for the existence of an asymptotic self-similar spreading regime dominated by thermal noise \cite{10}. By tuning the magnitude of the noise term, we could observe the cross over from the classical Tanner’s law, where the drop’s base radius $b$ grows with time as $b \sim t^{1/10}$ and the noise dominated regime where $b \sim t^{1/6}$. The observed scaling exponent is found to be more robust (regarding parameter selection) in the noise dominated case than for purely deterministic dynamics.

Presently, only the effect of thermal fluctuations on spreading has been studied. However, it is well known that fluids at the nanoscale are also strongly influenced by van der Waals interactions (disjoining pressure). It was argued in \cite{10} that, for complex fluids, these effects are negligible at least in a certain parameter region due to their weaker van der Waals interactions. Furthermore, complex fluids are usually governed by non-Newtonian constitutive relations and it is not clear how these effects will influence spreading. This will be an interesting aspect to study in the future.

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