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On thermal fluctuations in thin film flow

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Abstract

In bulk fluids hydrodynamic Navier–Stokes equations are proven to be valid down to the nanometre scale. However, during the dewetting process of thin liquid films of nanometre thickness the interplay of surface tension γ , substrate potential and thermal noise can lead to qualitatively different behaviour on laterally much larger scales up to microns. By deriving a stochastic thin film equation with a conserved noise term we show that the spectrum of capillary waves changes from an exponential decay to a power law $k_B T / (\gamma q^2)$ for large wavevectors q due to thermal fluctuations at temperature T . Also the time evolution of film roughness $\sigma(t)$ and of the typical wavevector $k(t)$ of unstable perturbations changes qualitatively. Whereas a deterministic Navier–Stokes equation in the lubrication approximation predicts in the linear regime a constant $k(t) = k_0$, one finds a coarsening $k^2(t) - k_0^2 \sim \frac{k_B T}{\gamma \sigma^2(t)}$ due to thermal noise.

1. Noisy hydrodynamics of thin liquid films

In bulk fluids hydrodynamic Navier–Stokes equations are proven to be valid down to the nanometre scale, and up to now thin film flow has only been studied by deterministic equations [1]. However, during the dewetting process of thin liquid films of nanometre thickness [2–4] the interplay of substrate potentials and thermal noise may cause a qualitatively different behaviour on laterally much larger scales up to microns. In particular, for the further development of efficient tools that will be used in the design of microfluidic devices or electronic components whose function relies on thin film properties, it is essential to gain a quantitative understanding of thermal fluctuations during dewetting and its interplay with molecular interactions. To this end we derive here a stochastic version of the thin-film equation based on the lubrication approximation for incompressible hydrodynamic equations [5].

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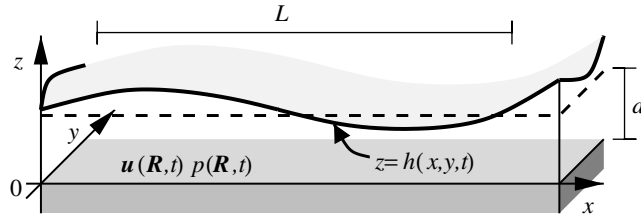


Figure 1. A thin liquid film on a flat substrate (coinciding with the xy -plane). The film surface (i.e., the moving boundary) is parametrized by the film thickness $h(x, y, t)$. The flow is characterized by the flow velocity $\mathbf{u} = (u_x, u_y, u_z)$ and the pressure p as a function of $\mathbf{R} = (x, y, z)$ and t . The dashed line indicates the mean film thickness d which is small as compared to any lateral length scale L .

We consider a film of an incompressible Newtonian liquid on an infinite flat substrate at the xy -plane as shown in figure 1. Assuming that the film surface has no overhangs, we parametrize it by the thickness $h(\mathbf{r}, t)$ with $\mathbf{r} = (x, y)$. Momentum conservation leads to the Navier–Stokes equation [5]

$$\rho \frac{\partial \mathbf{u}}{\partial t} + \mathbf{u} \cdot \nabla_3 \mathbf{u} = \mu \nabla_3^2 \mathbf{u} - \nabla_3(p - \Pi) + \nabla_3 \cdot \mathbf{S}, \quad (1)$$

and mass conservation to the incompressibility condition $\nabla_3 \cdot \mathbf{u} = 0$. By \mathbf{u} and p , we denote velocity and pressure field, respectively, and by $\nabla_3 = (\nabla_x, \nabla_y, \nabla_z)$ the three-dimensional gradient operator. The mass density ρ is constant and μ is the shear viscosity. The random stress fluctuations \mathbf{S} represent the effect of molecular motion. \mathbf{S} is symmetric, has zero mean $\langle \mathbf{S} \rangle = 0$ and the correlator is

$$\langle S_{ij}(\mathbf{R}, t) S_{lm}(\mathbf{R}', t') \rangle = 2k_B T \mu \delta(\mathbf{R} - \mathbf{R}') \delta(t - t') (\delta_{il} \delta_{jm} + \delta_{im} \delta_{jl}), \quad (2)$$

with the thermal energy $k_B T$. $\Pi = -\frac{\partial \Phi(h)}{\partial h}$ is the so-called disjoining pressure, namely the negative derivative of the effective interface potential $\Phi(h)$ with respect to the film thickness h . The origins of the disjoining pressure are molecular interactions among liquid molecules as well as between the liquid and the substrate molecules. The disjoining pressure determines the wetting properties of a substrate such as the equilibrium contact angle. We assume that the substrate is impermeable and that there is no slip between the fluid and the substrate. The boundary condition at the substrate is therefore $\mathbf{u} = 0$ at $z = 0$. At the free surface $z = h(\mathbf{r}, t)$ the normal and tangential stresses are balanced. Neglecting the vapour the boundary condition is

$$(\boldsymbol{\sigma} + \mathbf{S}) \cdot \hat{\mathbf{n}} = \kappa \gamma \hat{\mathbf{n}}, \quad (3)$$

where $\sigma_{ij} = \mu(\nabla_i u_j + \nabla_j u_i) - p \delta_{ij}$ is the stress tensor for an incompressible fluid, κ is the mean curvature of the surface, $\hat{\mathbf{n}} = (-\nabla h, 1)/\sqrt{1 + (\nabla h)^2}$ is the surface normal vector, and γ is the surface tension coefficient. With $\nabla = (\nabla_x, \nabla_y)$ we denote the two-dimensional gradient operator. Finally, assuming that the fluid is non-volatile, the component of the flow velocity normal to the surface is identical to the surface normal velocity and we get with $\mathbf{u}_{\parallel} = (u_x, u_y)$

$$\frac{\partial h}{\partial t} = u_z|_{z=h} - \mathbf{u}_{\parallel}|_{z=h} \cdot \nabla h = -\nabla \cdot \int_0^{h(\mathbf{r}, t)} \mathbf{u}_{\parallel}(\mathbf{r}, z, t) dz. \quad (4)$$

2. Lubrication approximation of stochastic Navier–Stokes equation

For a smooth thin film, where the ratio $\varepsilon = d/L$ of the characteristic film height d is much smaller than the length scale L over which the film thickness and substrate properties (e.g., Π)

vary laterally (see figure 1), one can find an approximate solution for the free boundary flow. This approach is well described in [1] so we focus here only on the noise term \mathbf{S} . For details we refer to [6]. In order to implement this long wavelength expansion we non-dimensionalize equations (1)–(4). Denoting a characteristic velocity in the film parallel to the substrate by U , we use the rescaling relations $\mathbf{r} = L\tilde{\mathbf{r}}$, $z = d\tilde{z}$, $t = \frac{L}{U}\tilde{t}$ and

$$S_{iz} = \frac{U\mu}{d}\tilde{S}_{iz}, \quad (S_{ij}, S_{zz}) = \frac{U\mu}{L}(\tilde{S}_{ij}, \tilde{S}_{zz}), \quad \text{for } i, j \in \{x, y\}. \quad (5)$$

Thereby, we assume that the components of the noise tensor scale like the dominant term (lowest order in ε) in the corresponding components of the trace-less part of the stress tensor $\boldsymbol{\sigma}$. We furthermore balance viscous and capillary forces with disjoining pressure by choosing $\gamma = \frac{U\mu}{\varepsilon^3}\tilde{\gamma}$ and $(p, \Pi) = \frac{U\mu}{d\varepsilon}(\tilde{p}, \tilde{\Pi})$. The dimensionless temperature (or noise amplitude) is $\tilde{T} = \frac{k_B T d}{\mu U L^3}$. This way, the noise tensor will appear in the lowest order equations of motion in such a way that the stationary height distribution of the resulting thin-film equation (7) is the one required by thermodynamics. This justifies this rescaling retrospectively. In addition to $\varepsilon \ll 1$ we assume that the Reynolds number $Re = \rho U d / \mu$ is small.

In order to avoid clumsy notation we drop the tilde in the following and use dimensionless quantities only. Then, we get for the parallel and normal components of the momentum equation (1)

$$0 = -\nabla(p - \Pi) + \nabla^2 \mathbf{u}_{\parallel} + \nabla \cdot \mathbf{S}_{z\parallel} \quad \text{and} \quad 0 = -\nabla_z(p - \Pi), \quad (6)$$

with $\mathbf{S}_{z\parallel} = (S_{zx}, S_{zy})$. The incompressibility condition, the boundary conditions at the substrate as well as the kinematic condition (4) remain unchanged under these rescalings. From the normal and tangential components of equation (3) we get $p = -\gamma \nabla^2 h$ for the pressure at the liquid–vapour interface and $\nabla_z \mathbf{u}_{\parallel} + \mathbf{S}_{z\parallel} = 0$ for the velocity at $y = h$, respectively. We can integrate these equations with the same technique as used in the deterministic case and get the following stochastic thin-film equation:

$$\frac{\partial h}{\partial t} = \nabla \cdot \left\{ \frac{h^3}{3} \nabla [\Phi'(h) - \gamma \nabla^2 h] + \int_0^h (h - y) \mathbf{S}_{z\parallel}(y) dy \right\}. \quad (7)$$

The noise term in equation (7) is of a rather complicated form. It is a sum of uncorrelated noise terms integrated over the film thickness and it is a conserved noise term in the sense that it is the divergence of a random current. Additionally, in contrast to the thermal noise in the original hydrodynamic equation (1), the noise term in equation (7) is multiplied by the function $h(x, t)$ which depends on the noise, too. However, one can show (see [6] for details) that the Langevin equation

$$\frac{\partial h}{\partial t} = \nabla \cdot \left\{ \frac{h^3}{3} \nabla [\Phi'(h) - \gamma \nabla^2 h] + \sqrt{\frac{2T}{3}} h^3 \boldsymbol{\eta}(t) \right\}, \quad (8)$$

with a single multiplicative conserved noise vector $\boldsymbol{\eta}(\mathbf{r}, t)$ obeying the correlator

$$\langle \boldsymbol{\eta}(\mathbf{r}, t) \rangle = 0 \quad \text{and} \quad \langle \eta_i(\mathbf{r}, t) \eta_j(\mathbf{r}', t') \rangle = \delta_{ij} \delta(\mathbf{r} - \mathbf{r}') \delta(t - t') \quad (9)$$

has the same corresponding Fokker–Planck equation, i.e., the same time evolution of the height-distribution function $\mathcal{W}[h]$. Equation (8) is therefore to be considered identical to equation (7). Moreover, the distribution function fulfilling the detailed balance condition is given by

$$\mathcal{W}_{\text{eq}}[h] = \mathcal{Z}^{-1} \exp\left(-\frac{1}{T} \mathcal{H}[h]\right) \quad \text{with} \quad \mathcal{H}[h] = \int dx \left[\Phi(h) + \frac{\gamma}{2} |\nabla_x h|^2 \right] \quad (10)$$

and the partition function \mathcal{Z} as expected from thermodynamics. $\mathcal{H}[h]$ is the effective interface Hamiltonian.

In order to estimate the dimensionless amplitude T of the noise, we consider the system studied in [4], i.e., a polystyrene (PS) film of thickness $d \approx 4$ nm on silicon dioxide. In this case, the thin liquid film is linearly unstable and the characteristic lateral length scale is given by the dispersive capillary length $L = 4\sqrt{\frac{\pi^3\gamma d^4}{A}}$. With the Hamaker constant $A \approx 2 \times 10^{-20}$ N m and the surface tension coefficient $\gamma \approx 3 \times 10^{-2}$ N m⁻¹ we have $L \approx 400$ nm. The Hamaker constant determines the disjoining pressure ($\Pi(h) = -\frac{A}{6\pi h^3}$ in dimensional quantities) if we neglect the short ranged part of the potential. The viscosity is $\mu \approx 1200$ N s m⁻². In the deterministic part of equation (8) there are two terms which can drive the flow, the disjoining pressure and the surface tension. The flow associated with each part is of the order of dU and from this we derive two characteristic velocities, namely $U_\Pi = \frac{A}{6\pi d L \mu} \approx 0.6$ nm s⁻¹ and $U_\gamma = \frac{d^3\gamma}{3L^3\mu} \approx 8 \times 10^{-3}$ nm s⁻¹, respectively. We take the larger of the two velocities and therefore $U \approx 0.6$ nm s⁻¹. According to equation (5), with this choice of U the dimensionless disjoining pressure has no free parameter $\Pi(h) = -\frac{1}{h^3}$ and the noise amplitude T is given by $\frac{3k_B T}{8\pi^2 d^2 \gamma}$ (in dimensional quantities). The experiments were performed at 53 °C, which leads to $T \approx 4 \times 10^{-4}$.

The noise induced current is therefore about two orders of magnitude smaller than the current induced by the disjoining pressure. However, in numerical studies one finds that the noise term accelerates the initial dynamics of thin polymer films by at least a factor of five, if realistic values are chosen for surface tension, substrate potential, and viscosity [6]. Since fluctuations are most important in the early stages of dewetting, i.e., before film rupture, we can quantify the influence of the noise by analysing the linearized version of equation (8) for a spinodally unstable film.

3. Linear approximation of the stochastic thin film equation

At the beginning of the dewetting process the deviations $\delta h(\mathbf{r}, t) = h(\mathbf{r}, t) - h_0$ from the initial film height h_0 are small. By expanding equation (8) in first order of δh and η (assuming that the noise amplitude is small as well) we obtain the linear stochastic equation

$$\frac{\partial \delta h(\mathbf{r}, t)}{\partial t} = \frac{h_0^3}{3} [\Phi''(h_0) \nabla^2 \delta h(\mathbf{r}, t) - \gamma \nabla^4 \delta h(\mathbf{r}, t)] + \sqrt{\frac{2Th_0^3}{3}} \nabla \cdot \eta(t) \quad (11)$$

with $\Phi''(h_0) < 0$. Note that the multiplicative noise in equation (8) becomes additive so the solution can be obtained straightforwardly by Fourier transformation $\delta h(\mathbf{r}, t) = \int \frac{d^2 q}{(2\pi)^2} \tilde{\delta h}(\mathbf{q}, t) e^{i\mathbf{q} \cdot \mathbf{r}}$. This yields

$$\frac{\partial \tilde{\delta h}(\mathbf{q}, t)}{\partial t} = \omega(\mathbf{q}) \tilde{\delta h}(\mathbf{q}, t) + i \sqrt{\frac{2Th_0^3}{3}} \mathbf{q} \cdot \tilde{\eta}(\mathbf{q}, t). \quad (12)$$

The dispersion relation $\omega(\mathbf{q}) = [1 - (q^2/q_0^2 - 1)^2]/t_0$ has a maximum at the wavevector $q_0^2 = -\Phi''(h_0)/(2\gamma)$ and a characteristic time $t_0 = 3/(\gamma h_0^3 q_0^4)$. With this the Fourier transform of the height–height correlation function reads $\langle \tilde{\delta h}(\mathbf{q}, t) \tilde{\delta h}(\mathbf{q}', t') \rangle = (2\pi)^2 \delta(\mathbf{q} + \mathbf{q}') \tilde{C}(|\mathbf{q}|; t, t')$ with

$$\tilde{C}(\mathbf{q}; t, t') = \tilde{C}_0(\mathbf{q}) e^{\omega(\mathbf{q})(t+t')} + \frac{Th_0^3}{3} \frac{q^2}{\omega(\mathbf{q})} [e^{\omega(\mathbf{q})(t+t')} - e^{\omega(\mathbf{q})|t-t'|}] \quad (13)$$

for $t, t' \geq 0$ and the initial power spectrum $\tilde{C}_0(\mathbf{q}) = \langle |\tilde{\delta h}(\mathbf{q}, 0)|^2 \rangle$ at $t = 0$. Note that the dispersion relation $\omega(\mathbf{q})$ is negative for $q > \sqrt{2}q_0$; see the inset in figure 2. In the long time limit

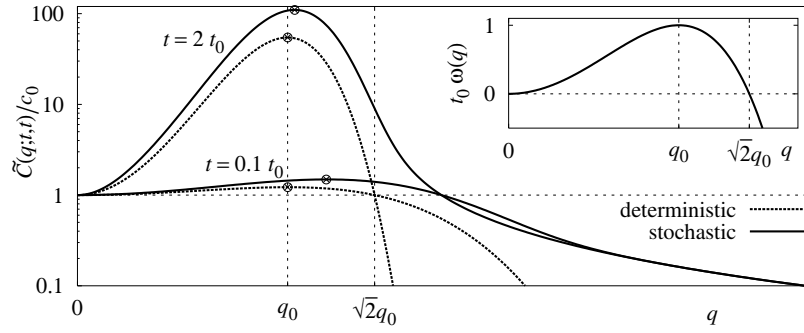


Figure 2. Power spectrum of a spinodally dewetting film with (solid line) and without noise (dashed line), for $T = \gamma q_0^4 c_0$ for two different times $t = 0.1 t_0$ and $t = 2.0 t_0$, cf equation (13). The initial spectrum at $t = 0$ is $\tilde{C}(q; 0, 0) = c_0$. The maxima are marked with circles. The inset shows the dispersion relation $\omega(q)$.

$t = t' \rightarrow \infty$ one finds exponential decay $\tilde{C}(q; t, t) \rightarrow \tilde{C}_0(q) e^{-2|\omega(q)|t}$ for the deterministic dynamics ($T = 0$) but the algebraic capillary wave spectrum $\tilde{C}(q; t, t) \rightarrow \frac{T h_0^3}{3} \frac{q^2}{|\omega(q)|} \rightarrow \frac{T}{\gamma q^2}$ for any finite T . Note that for sufficiently small initial roughness and temperature T one is still in the linear regime for $t > t_0$. The time evolution of the power spectrum with and without noise for a white initial spectrum $\tilde{C}(q; 0, 0) = c_0$ is shown in figure 2. For large q the stochastic spectrum is at a steady state. Note that the maximum of the deterministic spectrum stays at q_0 for all times but the maximum of the stochastic spectrum approaches q_0 from above as $t \rightarrow \infty$. This noise generated coarsening process can last until non-linearities become important, effectively masking the typical feature of the linear deterministic regime, namely that the maximum of the power spectrum stays at a fixed wavenumber.

At this point we note that the spectrum necessarily has a microscopic cut-off $q_{\max} \gg q_0$ at the scale of the fluid particles. For simplicity we assume equation (13) holds up to this point and $\tilde{C}(q; t, t) = 0$ for $q > q_{\max}$. In order to illustrate further the spatial features of the dynamics we calculate the roughness of the film, i.e., the variance $\sigma^2(t) = \langle [\delta h(\mathbf{r}, t)]^2 \rangle$, as well as the variance of the local slope $k^2(t) = \langle [|\nabla \delta h(\mathbf{r}, t)|^2] \rangle / (2\pi \sigma^2(t))$ normalized to the roughness (which is a measure for the characteristic wavelength of fluctuations). For $\sigma^2(t)$ we get

$$\sigma^2(t) = \int \frac{d^2 q}{(2\pi)^2} \tilde{C}(q; t, t) = \sigma_{T=0}^2(t) + \frac{T}{4\pi\gamma} \int_{-1}^{\frac{q_{\max}^2}{q_0^2} - 1} d\theta \frac{1 - e^{-2\frac{t}{t_0}(\theta^2 - 1)}}{\theta - 1} \quad (14)$$

with the deterministic evolution $\sigma_{T=0}^2(t)$ of the roughness and the substitution $\theta = (q/q_0)^2 - 1$. In order to get analytical results we choose the initial spectrum $\tilde{C}_0(q) = c_0$ for $q < \sqrt{2}q_0$ and $\tilde{C}_0(q) = 0$ for $q > \sqrt{2}q_0$. This choice is computationally convenient but one can also imagine a preparation process which results in qualitatively similar initial conditions, i.e., with strongly suppressed short wavelength fluctuations. With this we get

$$\sigma_{T=0}^2(t) = \sigma_0^2 \sqrt{\frac{\pi t_0}{8t}} e^{2\frac{t}{t_0}} \operatorname{erf}\left(\sqrt{\frac{2t}{t_0}}\right), \quad \text{with } \operatorname{erf}(s) = \frac{2}{\sqrt{\pi}} \int_0^s dx e^{-x^2} \quad (15)$$

and the initial roughness $\sigma^2(0) = \sigma_0^2 = c_0 \frac{q_0^2}{2\pi}$. For large t we can calculate the ratio $\sigma^2(t)/\sigma_{T=0}^2(t) \rightarrow 1 + \Xi + \mathcal{O}(t^{-1})$ with $\Xi = \frac{T}{2\pi\gamma\sigma_0^2} > 0$. Note that Ξ is given by the ratio of the thermal (capillary) roughness T/γ over the initial roughness σ_0^2 . It is this ratio

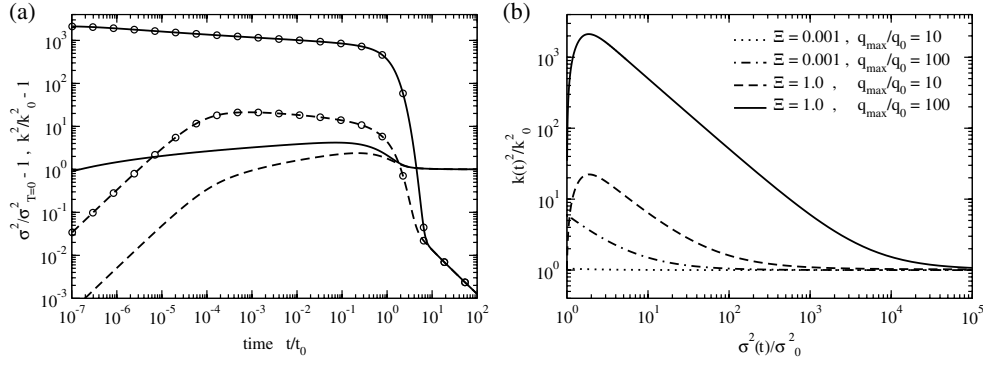


Figure 3. (a) Deviation of the roughness $\sigma^2(t)$ (lines) and the variance of local slopes $k^2(t)$ (lines with circles) from the deterministic value $\sigma_{T=0}^2(t)$ and from the initial value k_0^2 , respectively, for $\Xi = 1$ and $q_{\max}/q_0 = 10$ (dashed line) and 100 (solid line); see also the legend in (b). The influence of thermal noise is strongest at the beginning. For $t \gg t_0$, $k^2(t)$ goes back to its initial value while $\sigma^2(t)$ follows equation (14) but with a renormalized initial roughness (therefore the curves for $\sigma^2(t)$ converge to $\Xi = 1$). (b) $k^2(t)$ versus $\sigma^2(t)$ for $\Xi \in \{0.001, 1\}$ and $q_{\max}/q_0 \in \{10, 100\}$, both normalized to their initial values. Due to thermal noise $k^2(t)$ approaches the final value $k^2(t \rightarrow \infty) = k^2(0) = \frac{q_0^2}{2\pi}$ from above with $k^2(t)/k^2(0) - 1 \sim 1/\sigma^2(t)$ for any noise amplitude T as long as the characteristic wavelength $2\pi/q_0$ is much larger than the molecular cut-off $2\pi/q_{\max}$.

which determines the importance of thermal fluctuations for the dynamics of the film. One may argue that the initial roughness is due to a quenched thermal capillary wave spectrum so that one may expect Ξ to be of order unity. A numerical integration of equation (14) plotted in figure 3(a) shows that thermal noise is most important at the beginning of the process. One finds a fast linear increase $\sigma^2(t)/\sigma_{T=0}^2(t) = 1 + \frac{\Xi}{2}t/t_m + \mathcal{O}(t^2)$ of the thermal roughness with the characteristic (microscopic) time $t_m = \frac{q_0^4}{q_{\max}^4}t_0$ due to a rapid build-up of a thermal spectrum for $q > \sqrt{2}q_0$, followed by a slower increase for $t_m < t$ and up to t_0 due to the (linear) dewetting process. However, for times $t \gg t_0$ thermal fluctuations become less important compared to the exponential increase of the unstable mode q_0 and one reaches a ‘quasi’-deterministic behaviour with $\sigma^2(t)$ given by equation (15) but with a renormalized initial roughness $\sigma_0^2 + \frac{T}{2\pi\gamma}$.

For the variance of the local slope of the film height we find

$$\begin{aligned} k^2(t) &= \int \frac{d^2q q^2 \tilde{C}(q; t, t)}{(2\pi)^2 2\pi\sigma^2(t)} \\ &= \frac{q_0^2}{2\pi} \frac{\sigma_{T=0}^2(t)}{\sigma^2(t)} + \frac{Tq_0^2}{8\pi^2\gamma\sigma^2(t)} \int_{-1}^{\frac{q_{\max}^2}{q_0^2} - 1} d\theta \frac{\theta + 1}{\theta - 1} [1 - e^{-\frac{2\pi}{q_0}(\theta^2 - 1)}], \end{aligned} \quad (16)$$

with the initial and final value $k^2(0) = k^2(\infty) = \frac{q_0^2}{2\pi}$. Note that for the deterministic dynamics $k_{T=0}^2(t) = \frac{q_0^2}{2\pi}$ is constant in time for the chosen initial spectrum. However, for the stochastic dynamics $k^2(t)$ starts at the deterministic value at $t = 0$ and, as one can see in figure 3(a), increases linearly in time until it reaches a maximum at $t \approx t_m$ before approaching the deterministic value $k^2(t)/k^2(0) \rightarrow 1 + \frac{\Xi}{1+\Xi} \frac{t_0}{4t} + \mathcal{O}(t^{-2})$ from above for $t \gg t_0$. If the microscopic cut-off q_{\max} is much larger than q_0 , one obtains an intermediate time regime $t_m < t$ up to $t \approx t_0$ where the integral in equation (16) is approximately constant and one gets

$$k^2(t)/k^2(0) \approx 1 + \frac{\Xi}{2} \frac{q_{\max}^2}{q_0^2} \frac{\sigma_0^2}{\sigma^2(t)}. \quad (17)$$

The numerical results for equation (16) shown in figure 3(b) as a function of $\sigma^2(t)$ confirm that $k^2(t)/k^2(0) - 1$ is indeed proportional to $1/\sigma^2(t)$ for intermediate times up to $t \approx t_0$. Thus, thermal noise generates coarsening even in the linear regime for which the deterministic linear dynamics predicts a fixed characteristic wavevector $k^2(t) = \frac{q_0^2}{2\pi}$. A separation of length scales $q_{\max} \gg q_0$ also leads to a separation of timescales $t_m = \frac{q_0^4}{\sigma_{\max}^4} t_0 \ll t_0$, so that the algebraic decrease of $k^2(t)$ with $\sigma^2(t)$ is visible, before the exponentially growing peak in the structure function (see figure 2) causes a crossover to an algebraic behaviour in time $k^2(t)/k_0^2 - 1 \sim 1/t$ for $t > t_0$. We expect the linear approximation in equation (11) to hold at least for the fast initial ($t < t_m$) formation of the thermal spectrum for $q > q_0$ as well as for the noise dominated spinodal dewetting process up to $t \approx t_0$.

Finally, one can conclude that the noise term in the structure function $\tilde{C}(q; t, t')$ is relevant for any value of the noise amplitude T , as long as the dispersion relation $\omega(q)$ becomes negative for large wavevectors $q_{\max} > q > \sqrt{2}q_0$. For realistic values for surface tension and substrate potentials one finds $L = 2\pi/q_0 \approx 0.1 \dots 1 \mu\text{m}$ (see the discussion at the end of section 2), which is much larger than the size of molecules which provides an upper cut-off q_{\max} for allowed wavevectors. Thus, the time evolution of $\sigma^2(t)$ and $k^2(t)$ given by equations (14) and (16), respectively, are always dominated by the thermal noise term for times $t < t_0$ up to the characteristic time t_0 of the fastest growing mode q_0 .

4. Summary

We derived a stochastic version of the thin-film equation based on the lubrication approximation for incompressible hydrodynamic equations [5] and demonstrated its thermodynamic consistency, in particular with the equilibrium distribution of film thickness. The stochastic equation (8) with a conserved noise term can be used to investigate the influence of thermal fluctuations on (de)wetting dynamics of unstable liquid films which has been studied extensively in the last decades [2–4], but theoretically solely by deterministic dynamical equations. However, thermal noise gains a more and more important role the smaller the system size becomes. Recent numerical studies of thin film evolution indicate that thermal noise might influence characteristic timescales of the dewetting process [6]. A linear approximation indicates that the spectrum of capillary waves changes from an exponential decay to a power law for large wavevectors due to thermal fluctuations. Consequently, the time evolution of the film roughness $\sigma^2(t) = \langle \delta h(\mathbf{r}, t) \delta h(\mathbf{r}, t) \rangle$ and also of the typical wavelengths of the maximum of the power spectrum are found to change qualitatively. Whereas the deterministic equation predicts a constant wavelength, the stochastically evolving structures coarsen in time and $\sigma^2(t)$ is expected to increase much faster due to the thermal noise. These consequences of the stochastic nature of the thin film dynamics are robust, i.e., the failure of the deterministic hydrodynamic description due to thermal fluctuations is expected already for small noise amplitudes in thin liquid films and for a large class of substrate interactions. These theoretical predictions seem to be confirmed in recent AFM measurements of spinodal dewetting of thin polymer films [7] and may explain discrepancies between experiments and simulations, which are based on the deterministic Navier–Stokes equation [4]. The theory may also explain the rapid build-up of spinodal fluctuations which was found in liquid gold films [2, 3], where spinodal dewetting was observed for the first time. Furthermore the power spectrum of fluctuations should be accessible by scattering techniques. Thus, it is desirable to develop numerical solutions for equation (8) beyond the linear approximation and to compare the theoretical predictions with experiments. In the course of miniaturization of electronic and microfluidic devices a fully quantitative description of Newtonian liquids at surfaces is

essential and requires quantitative stochastic modelling of ultrathin film dynamics as well as mathematically well controlled numerical schemes which will be presented elsewhere [6].

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