Thermal fluctuations of an interface near a contact line

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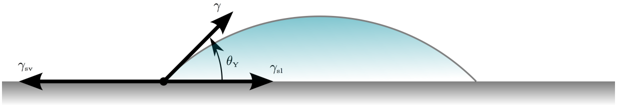
Introduction

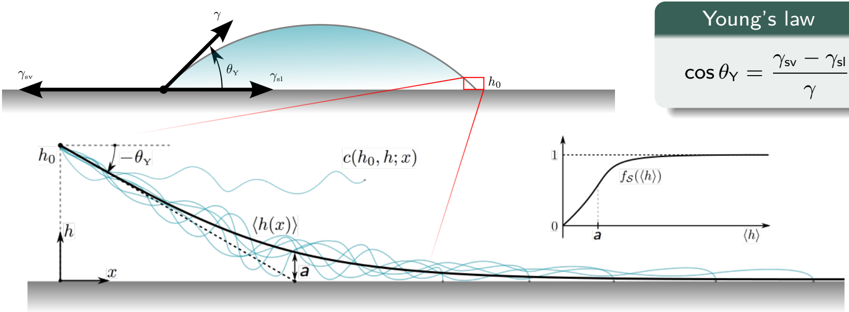
- The understanding and modelling of the dynamics of **wetting and contact lines**, such as spreading or motion of a droplet on a solid surface, is a subject at the forefront of physics, chemistry, and engineering;
- The **regularization** at the contact line is an essential ingredient: within all the descriptions provided in the literature, the physics near the contact line is **oversimplified** since **thermal fluctuations are ignored**;
- Our goal is to **start a different line of thought** to investigate **fluctuating contact lines** at the microscopic scale:
  1) **How thermal fluctuations behave** close to a contact line?
  2) **Thermal fluctuations alone** can provide any form of **microscopic regularization** within a purely local fluctuating hydrodynamic framework?
- The first step is then to consider a **static contact line** on a homogeneous substrate in presence of **thermal fluctuations**.



Young's law

$$\cos\theta_Y = \frac{\gamma_{sv} - \gamma_{sl}}{\gamma}$$

Mathematical framework



Young's law

$$\cos\theta_Y = \frac{\gamma_{sv} - \gamma_{sl}}{\gamma}$$

Profile probability

$$P_R[h] \propto e^{-\theta_Y^2 \frac{R}{2\ell}} e^{-\frac{1}{2\ell}\int_0^R \mathrm{d}x\, h'(x)^2}$$

- Take the thermodynamic limit, i.e. $R \to \infty$;
- Study the average profiles, i.e. $\langle h(x) \rangle$;
- Quantify the thermal regularization, i.e. a. Nope

Thermal lenght

$$\ell = k_B T/\gamma$$

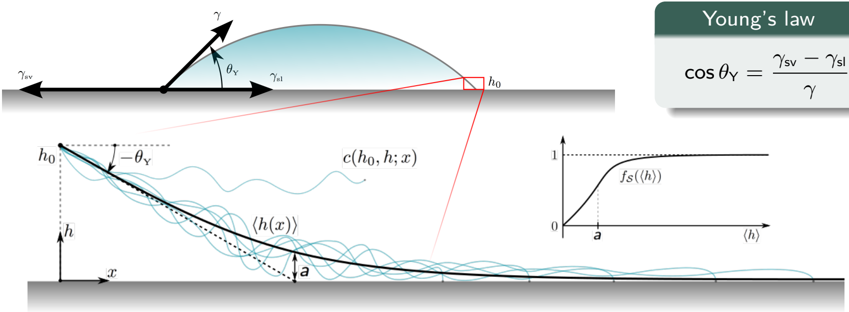
Partition function

$$Z_R = e^{-\theta_Y^2 \frac{R}{2\ell}} \int_{h(0)=h_0}^{h(R)=0} \mathcal{D}_\theta h\, e^{-\frac{1}{2\ell}\int_0^R \mathrm{d}x\, h'(x)^2}$$

Impenetrability

$$\ell\,(\partial \ln c/\partial h)_{h=0} = -\theta$$

Mathematical framework



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$$\cos\theta_{\mathrm{Y}} = \frac{\gamma_{\mathrm{sv}} - \gamma_{\mathrm{sl}}}{\gamma}$$

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$$P_R[h] \propto e^{-\theta_{\mathrm{Y}}^2 \frac{R}{2\ell}}\, e^{-\frac{1}{2\ell}\int_0^R \mathrm{d}x\, h'(x)^2}$$

- Study the statistics of the contact point, i.e. $P(R)$;
- Study the average profiles, i.e. $\langle h(x) \rangle$;
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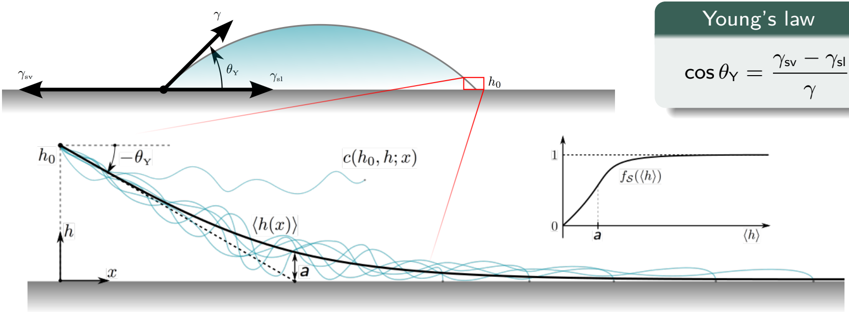

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Two dimensionless parameters

- $\mathcal{S} = \theta_Y h_0/\ell$ (scale separation): tells us how much thermal fluctuations can distort the interface;
- $\tau = \theta/\theta_Y$ (intensity of interactions): it parametrizes the microscopic binding effects close to the solid substrate.

Thermal lenght

$$\ell = k_B T/\gamma$$

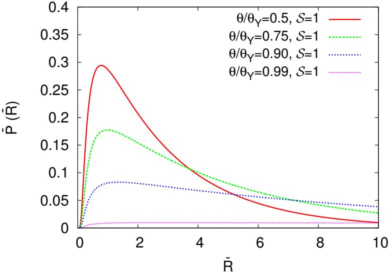
Impenetrability

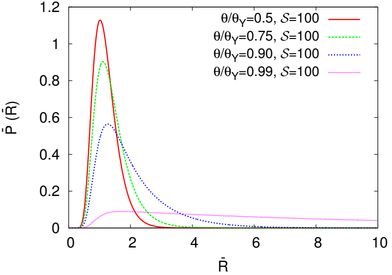
$$\ell\,(\partial \ln c/\partial h)_{h=0} = -\theta$$

Statistics of the contact point

Contact point probability

$$P(R) = \frac{1-\tau}{2}\left[\sqrt{\frac{2\mathcal{S}}{\pi R}}e^{\mathcal{S}(1-\frac{R}{2}-\frac{1}{2R})} + \tau\mathcal{S}e^{\mathcal{S}(1-\tau)[1-(1+\tau)\frac{R}{2}]}\,\mathrm{erfc}\left(\frac{1-\tau R}{\sqrt{2R/\mathcal{S}}}\right)\right]$$





Average contact point

$$\langle R\rangle = 1 + \frac{1}{\mathcal{S}}\frac{1}{1-\tau}$$

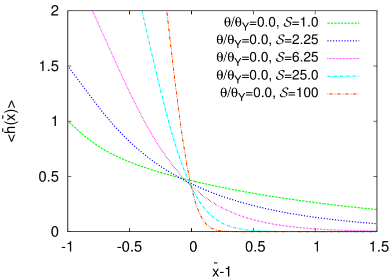
Variance

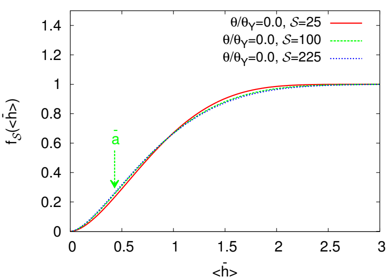
$$\delta R^2 = \frac{1}{\mathcal{S}}\left[1 + \frac{2-\tau}{\mathcal{S}(1-\tau)^2}\right]$$

Average profile and effective binding potential

Average profile

$$\langle h(x)\rangle = \frac{\tau}{(1+\tau)^2}\frac{e^{\mathcal{S}(1-\tau)[1-(1+\tau)\frac{x}{2}]}}{\sqrt{\mathcal{S}}}\,\mathrm{erfc}\left(\frac{1-\tau x}{\sqrt{2x/\mathcal{S}}}\right) - \frac{x-1}{2/\sqrt{\mathcal{S}}}\,\mathrm{erfc}\left(\frac{x-1}{\sqrt{2x/\mathcal{S}}}\right)$$
$$- \left[\frac{\tau}{(1+\tau)^2}\frac{1}{\sqrt{\mathcal{S}}} + \frac{1-\tau}{1+\tau}\frac{x+1}{2/\sqrt{\mathcal{S}}}\right] e^{2\mathcal{S}}\,\mathrm{erfc}\left(\frac{x+1}{\sqrt{2x/\mathcal{S}}}\right) + \frac{2}{1+\tau}\sqrt{\frac{x}{2\pi}}\,e^{-\frac{(x-1)^2}{2x/\mathcal{S}}}$$





Large x behavior

$$\langle h(x)\rangle \overset{x\to\infty}{\sim} \frac{1}{\sqrt{\mathcal{S}}}\frac{2\tau}{(1+\tau)^2}e^{\mathcal{S}(1-\tau)}e^{-\mathcal{S}(1-\tau^2)\frac{x}{2}}$$

Regularization lengthscale

$$a \overset{\mathcal{S}\to\infty}{\sim} \frac{1}{\sqrt{2\pi}}\sqrt{\frac{\ell h_0}{\theta_Y}}$$

Conclusions

- We have investigated the **effect of thermal fluctuations** on the morphology of an interface **near a contact line** in the presence of an impenetrable wall;
- We have introduced the **right ensemble** (integration over R) where **Young's angle is robust**, and the **inner physics** depends on a boundary condition parameter θ that is related to the microscopic deviation from Young's angle;
- The impenetrable nature of the boundary leads to a "repulsion" of capillary waves from the wall and the interactions between the fluctuating interface and the wall are captured in terms of an **effective binding potential** of finite range, **solely induced by thermal fluctuations**;
- **Pseudo-partial wetting states** are recovered in the limit $\theta \to \theta_{\mathrm{Y}}$;
- **Open issue**: Derivation of θ from inner model. Then, and then only, we may expect to predict the conditions under which a pseudo-partial wetting transition can be observed in a real three-dimensional case.

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Thanks for your attention!