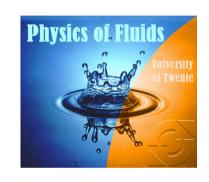
#### contact angle hysteresis

Jacco Snoeijer

Physics of Fluids - University of Twente

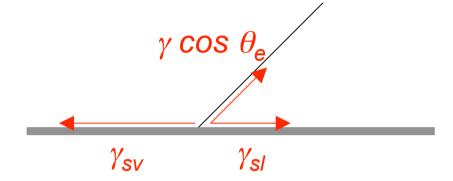




small droplets can 'stick' to window

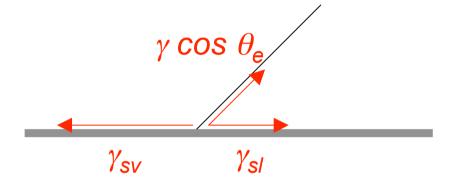
### force on contact line

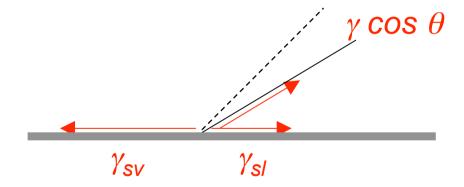
#### balance:



#### force on contact line

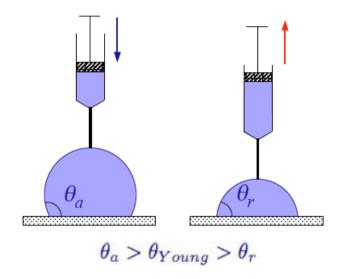
#### balance:





force on contact line:  $f_{cl} = \gamma (\cos \theta - \cos \theta_e)$ 

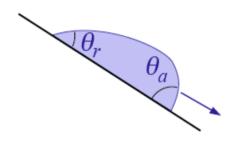
## advancing - receding angles



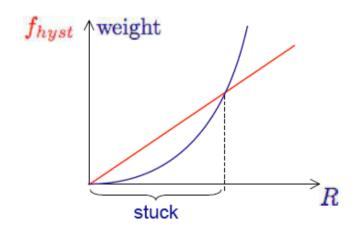
hysteresis: no unique value for contact angle

pinning force:  $H = \gamma (\cos \theta_r - \cos \theta_a)$ 

## 'sticky' drops

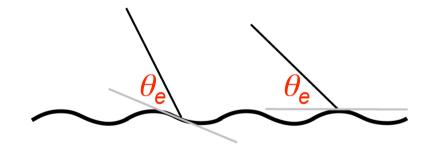


$$f_{hyst} \sim R\gamma \left(\cos \theta_r - \cos \theta_a\right)$$
  
weight  $\sim R^3 \rho g \sin \alpha$ 



## microscopic origin

geometric heterogeneity

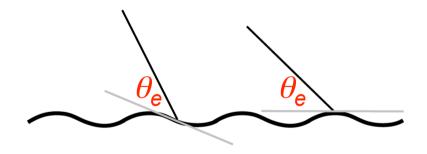


small scale 'roughness'

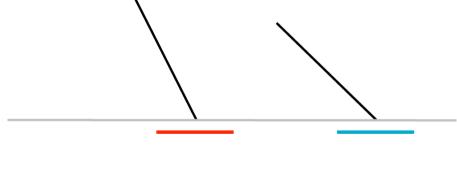
## microscopic origin

geometric heterogeneity

chemical heterogeneity:  $\theta_e(x,y)$ 



small scale 'roughness'



large  $\theta_e$ 

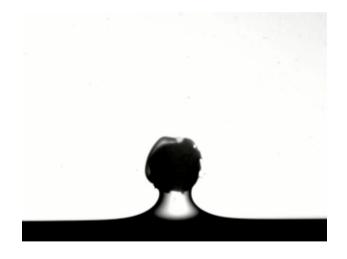
smaller  $\theta_{\rm e}$ 

# contact line shape?

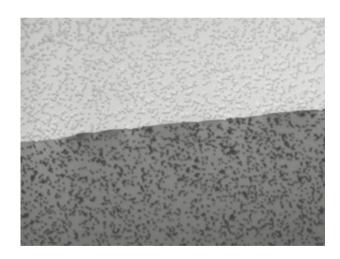
## contact line shape?

heterogeneity at larger scale: macroscopic 'wetting defects'

single defect (500µm)



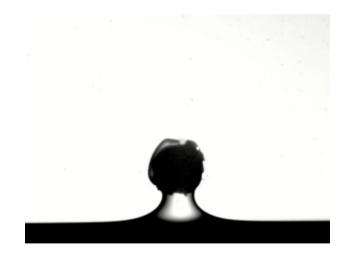
many defects (10μm)



### contact line shape?

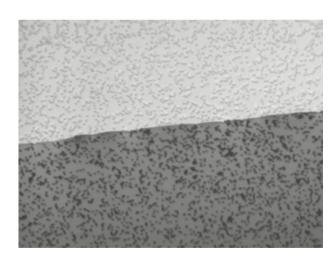
heterogeneity at larger scale: macroscopic 'wetting defects'

single defect (500µm)



'simple' dynamics

many defects (10μm)



collective dynamics contact line is very 'rough'

#### what will we do:

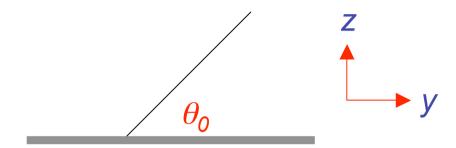
- contact line deformation of single defect
- Joanny De Gennes model for hysteresis
- implications for dynamics...

#### literature:

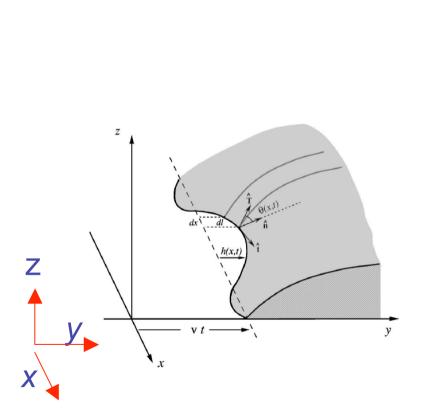
Joanny & De Gennes, J. Chem. Phys. **81**, 552 (1984)

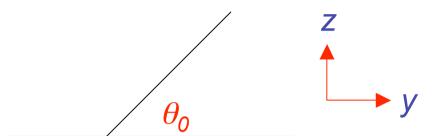
Bonn, Eggers, Indekeu, Meunier, Rolley, to appear Rev. Mod. Phys. (2009)

# contact line shape

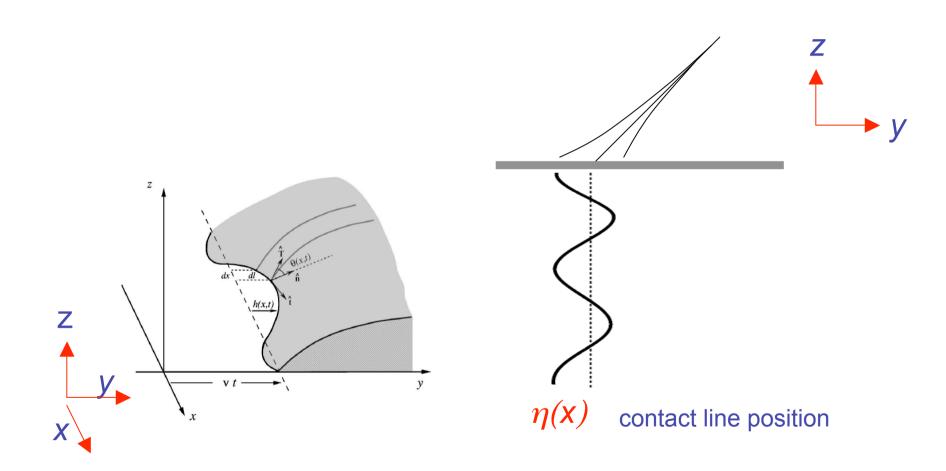


# contact line shape



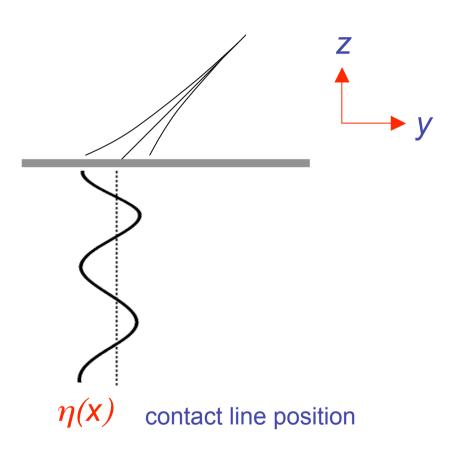


## contact line shape



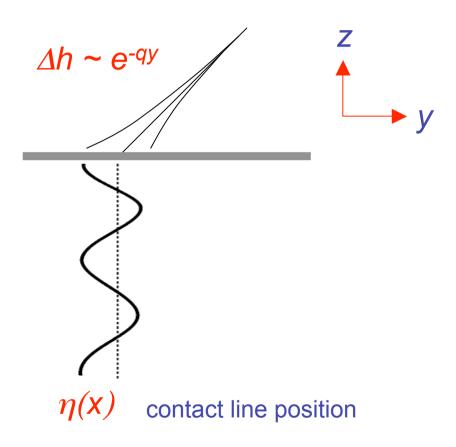
interface h(x,y)?

$$h(x,y) = \theta_0 y + \dots$$



interface h(x,y)?

$$h(x,y) = \theta_0 y + A e^{iqx} e^{-qy}$$



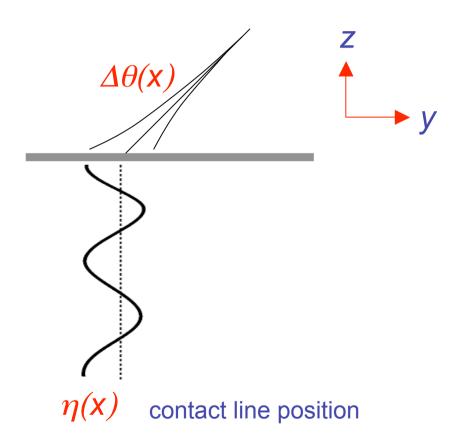
change in local contact angle:  $\Delta\theta(x)$   $\eta(x) \qquad \text{contact line position}$ 

increase of area

$$\Delta E \sim \gamma q A^2$$

contact line 'elasticity'

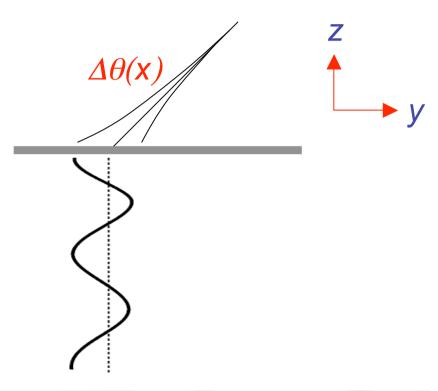
Joanny & De Gennes 1984

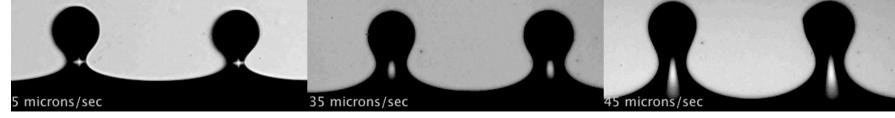


## sinusoidal perturbations

#### increase of area:

$$\Delta E \sim \gamma q A^2$$



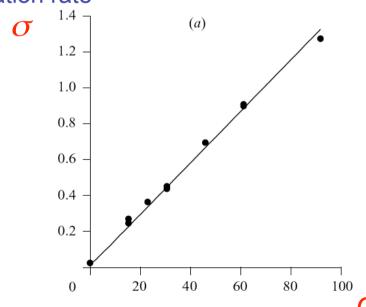


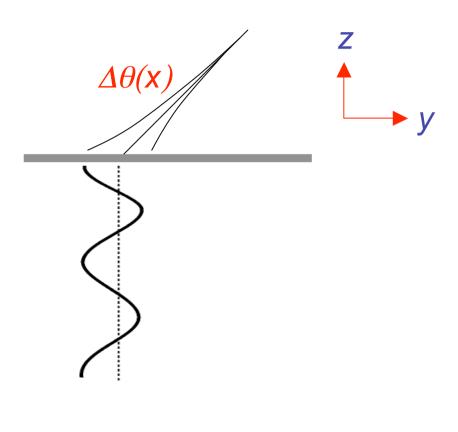
## sinusoidal perturbations

#### increase of area:

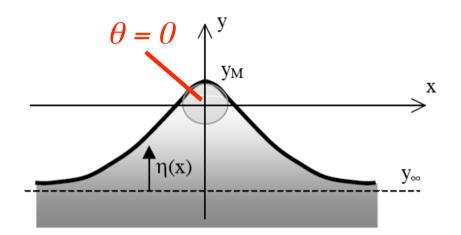
$$\Delta E \sim \gamma q A^2$$

#### relaxation rate



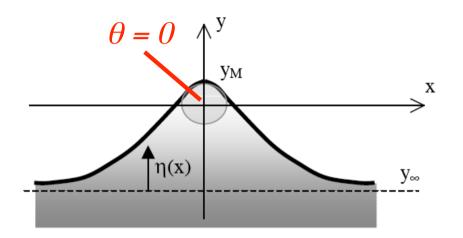


Delon et al. JFM 2008

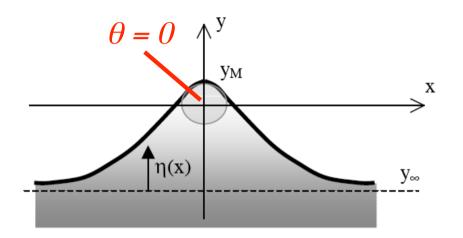


wetting defect is 'pulling', but....

large deformations cost energy

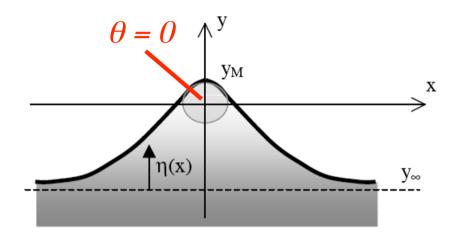


 $\eta(x)$  contact line shape ?



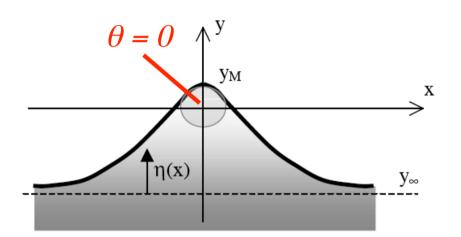
 $\eta(x)$  contact line shape?

$$h(x,y) = \theta_0 y + \dots$$



 $\eta(x)$  contact line shape?

$$h(x,y) = \theta_0 y - \frac{\theta_0}{2\pi} \int dq \, \tilde{\eta}(q) \, \underline{e^{iqx} e^{-qy}}$$

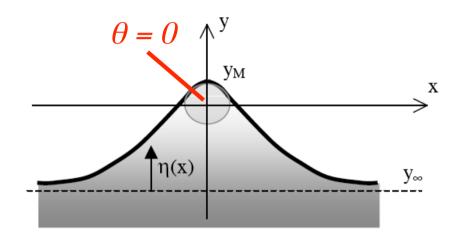


 $\eta(x)$  contact line shape ?

$$h(x,y) = \theta_0 y - \frac{\theta_0}{2\pi} \int dq \, \tilde{\eta}(q) \, \underline{e^{iqx} e^{-qy}}$$

imposing  $\theta(x)$  at the contact line

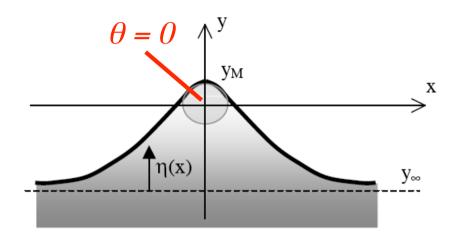
 $\eta(x)$ 



 $\eta(x)$  contact line shape?

$$h(x,y) = \theta_0 y - \frac{\theta_0}{2\pi} \int dq \, \tilde{\eta}(q) \, \underline{e^{iqx} e^{-qy}}$$

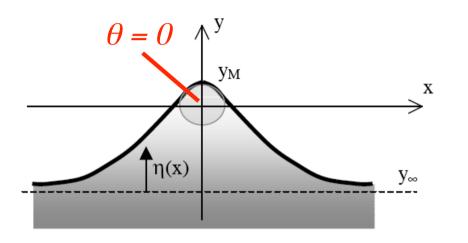
$$\theta \approx \frac{\partial h}{\partial y} = \theta_0 + \frac{\theta_0}{2\pi} \int dq \, \tilde{\eta}(q) \, \underline{q} \, e^{iqx} e^{-qy}$$



 $\eta(x)$  contact line shape?

$$h(x,y) = \theta_0 y - \frac{\theta_0}{2\pi} \int dq \, \tilde{\eta}(q) \, \underline{e^{iqx} e^{-qy}}$$

$$\theta(x) \approx \theta_0 + \frac{\theta_0}{2\pi} \int dq \left\{ \tilde{\eta}(q) \ q \right\} e^{iqx}$$



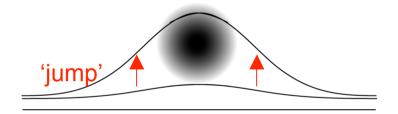
$$\eta(x) \sim \frac{F_{defect}}{\gamma} \ln(L/|x|)$$

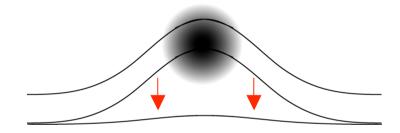
$$F_{defect} \sim d\gamma (1 - \cos \theta_e)$$

### model for hysteresis

advancing

receding



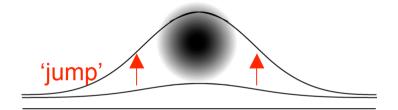


asymmetry between advancing and receding

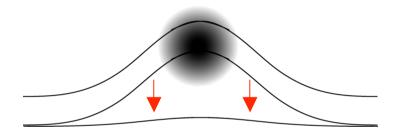
(for defects that are strong enough)

### model for hysteresis

#### advancing



#### receding



non-interacting defects, density  $\rho$ 

$$\gamma(\cos\theta_r - \cos\theta_a) \sim \rho F_d \eta_{\text{max}}$$

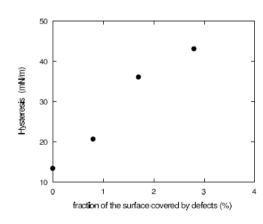
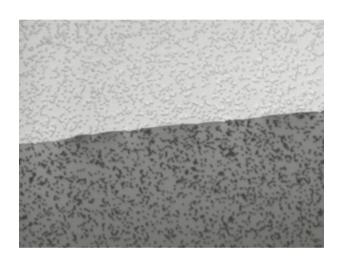
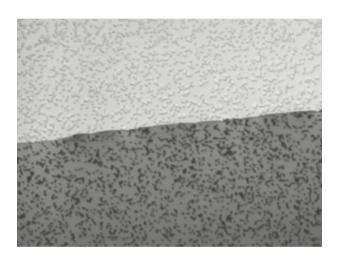


FIG. 48 Hysteresis as a function of the fraction X of the surface covered by defects (from Ramos *et al.* (2003)).

many defects (10μm)



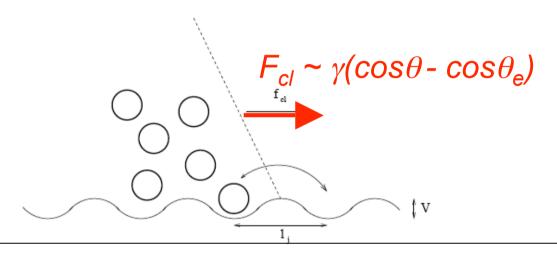
many defects (10μm)

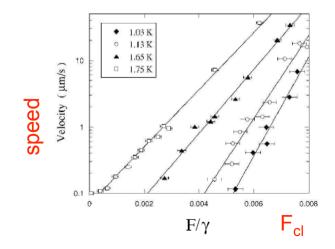


if we go very slowly...

... thermally activated 'hopping' of molecules

#### thermally activated 'hopping' of molecules

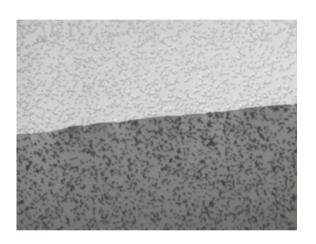


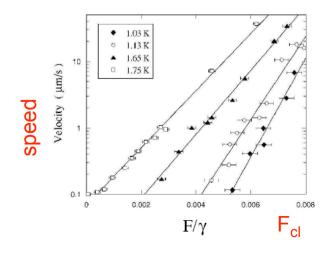


#### Rolley & Guthmann PRL 2007

$$U \sim \exp\left(-\frac{E - f_{cl} l_{micro}^2}{k_B T}\right)$$

#### thermally activated 'depinning' of contact line



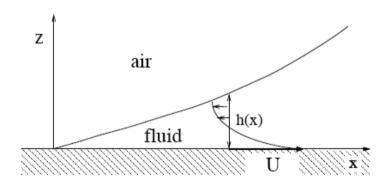


#### Rolley & Guthmann PRL 2007

$$U \sim \exp\left(-\frac{E - f_{cl} l_{micro}^2}{k_B T}\right)$$

## coupling to hydrodynamics?

for significant Ca: lubrication + slip



microscopics shows up as 'boundary conditions'

#### conclusion

- microscopic description of hysteresis
- 'interacting defects' are difficult...
  depinning, contact line roughness
- coupling to hydrodynamics??