

## Bridging the scales near the contact line

Len Pismen  
Technion, Haifa, Israel

### Outline

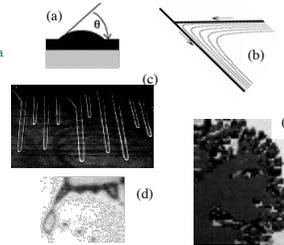
- ✓ A paradox resolved on nanoscale
- ✓ Approximation ladder: from DFT to lubrication equations
- ✓ Perturbation analysis: bridging the scales
- ✓ Applications: moving droplets

7/23/13

1

## Hydrodynamic problems involving moving contact lines

- (a) spreading of a droplet on a horizontal surface
- (b) pull-down of a meniscus on a moving wall
- (c) advancement of the leading edge of a film down an inclined plane
- (d) condensation or evaporation on a partially wetted surface
- (e) climbing of a film under the action of Marangoni force



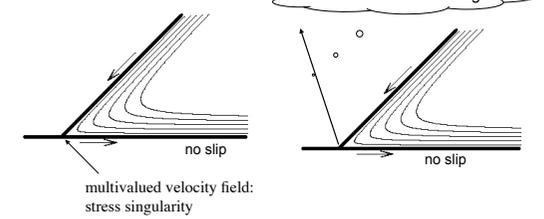
7/23/13

2

## Kinematic view: motion with no slip?

### Caterpillar advance

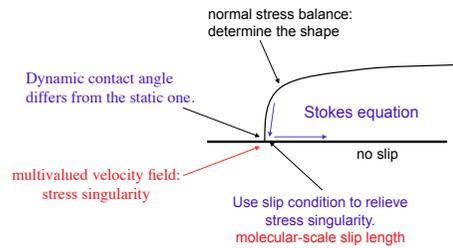
(angular shape... that's a problem)



7/23/13

3

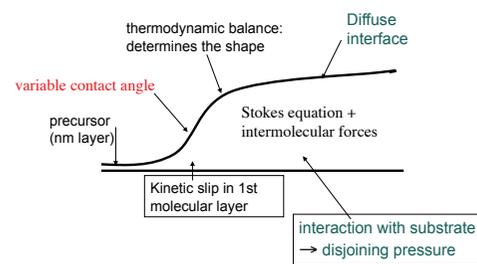
## Contact line paradox: Fluid-dynamical perspective



7/23/13

4

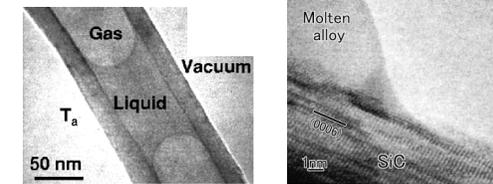
## Physico-chemical perspective



7/23/13

5

## Nanoscale experiments



TEM image of a capped carbon nanotube containing a liquid inclusion. C.M. Megaridis *et al.*, Appl. Phys. Lett. **70** 1021 (2001)

Spreading molten alloy C. Iwamoto and S. Tanaka Acta Materialia, **50** 749 (2002)

7/23/13

6

## Approximation ladder: Equilibrium

1. Write 3D free energy functional (e.g. vdW with hard-core cutoff)
2. Two-phase equilibrium: integrate along levels  $\rho = \text{const}$ ; obtain 1D functional with an integrated interaction kernel
3. Compute 1D density profile  $\rho(z-h)$  dependent on an arbitrary position  $h$  of the Gibbs surface; compute *surface tension*
4. Simplify the nonlocal equation to PDE? *What is lost?*
5. Introduce interaction with the substrate – compute *disjoining pressure*

8

## Thermodynamics – Energy functional

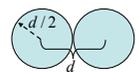
Helmholtz free energy per molecule of a fluid :

$$f[\rho(x)] = f_0 - \frac{T}{2} \int (e^{-U(r)/T} - 1) \rho(x+r) dr \quad (\text{start from stat. integral, reduce to pair interactions})$$

$U(r)$ : attractive part of hard core potential.

Homogeneous fluid: van der Waals interactions

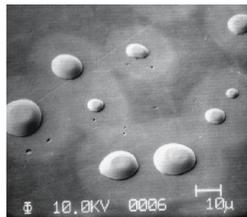
$$U(r) = \begin{cases} -\frac{A}{r^6} & \text{at } r > d \\ \infty & \text{at } r < d \end{cases} \quad \begin{array}{l} d \text{ is the nominal} \\ \text{hard-core molecular} \\ \text{diameter.} \end{array}$$



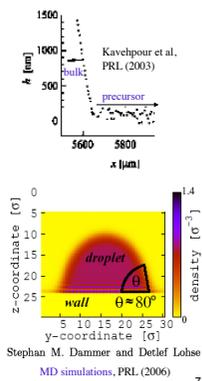
Approximation (LL v.5 §76):  $U/T \ll 1$  outside the hard core ( $r > d$ )

7/23/13

9



Photomicrograph of 3D Pb particles on a Cu(111) substrate taken in a SAM. Particles are surrounded by halos of the spreading 2D adsorbed phase J. Moon, J. Lowekamp, P. Wynblatt, S. Garoff and R. M. Suter, Surf. Sci. 488:73 (2001).



Stephan M. Dammer and Detlef Lohse MD simulations, PRL (2006)

7/23/13

7

### Liquid – vapour equilibrium

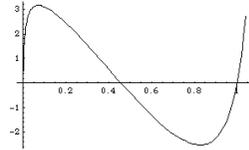
$$f[\rho(x)] = f_0 - \frac{T}{2} \int (e^{-U(r)/T} - 1) \rho(x+r) dr.$$

Homogeneous fluid: van der Waals equation of state ( $\rho = \text{const}$ )

$$\bar{f}(\rho, T) = T \ln \rho + \rho(bT - a) \approx T \ln \frac{\rho}{1 - b\rho} - a\rho$$

$b = \frac{2}{3} \pi d^3$ : excluded volume

$$a = -2\pi \int_d^\infty U(r) r^2 dr = \frac{2\pi A_l}{3d^3}$$



### Inhomogeneous fluid

Helmholtz free energy per molecule of a fluid :

$$f = \bar{f}(\rho, T) + \frac{1}{2} \int_{r>d} U(r') [\rho(r+r') - \rho(r)] dr' \Rightarrow F = \int \rho f dr$$

Homogeneous Inhomogeneous

The equilibrium density is enforced by the minimum of  $\Phi = F - \mu \int \rho dr$ .

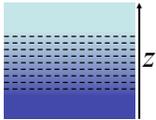
Euler-Lagrange equation for an inhomogeneous fluid:

$$g(\rho) - \mu + \int_{r>d} U(r) [\rho(x+r) - \rho(x)] d^3r = 0 \quad g(\rho) = d(\rho \bar{f}(\rho)) / d\rho$$

### 1D density profile

Construct 1D profiles across a planar interphase boundary by lumping interactions between layers  $z = \text{const}$

The 1D interaction kernel  $Q(z)$  lumps intermolecular interaction between layers  $z = \text{const}$ . It is computed by lateral integration using as an integration variable the squared distance  $q = r^2 = \xi^2 + z^2$ , where  $\xi$  is the radial distance in the lateral plane. Taking note that the lower integration limit for  $q$  is  $q_0 = z^2$  at  $|z| > d$ ,  $q_0 = d^2$  at  $|z| \leq d$ , we compute



$$Q(z) = -\pi A_l \int_{q_0}^\infty q^{-3} dq = \begin{cases} -\frac{1}{2} \pi A_l z^{-4} & \text{at } |z| > d \\ -\frac{1}{2} \pi A_l d^{-4} & \text{at } |z| \leq d. \end{cases}$$

Kirkwood & Buff; Yvon (1949)

### Inhomogeneous equilibrium density profile

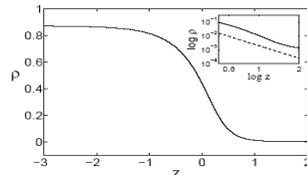
$$g(\rho) - \mu + \frac{3}{4} \beta \int Q(\xi) [\rho(z+\xi) - \rho(z)] d\xi = 0$$

in dimensionless units

$$\text{where } \beta = \frac{A_l}{k_s T d^6}, \quad Q(z) = \begin{cases} -\frac{1}{z^4} & \text{at } |z| > 1 \\ -1 & \text{at } |z| \leq 1 \end{cases}$$

Tail decay approximation at large distances from interface center ( $z=0$ ):

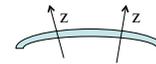
$$\rho = \rho_0^+ + \frac{\beta(\rho_0^+ - \rho_0^-)}{4g'(\rho_0^+)} \frac{1}{z^2}$$



surface tension

$$\gamma = \int_{-\infty}^\infty \rho(z) [\bar{f}(\rho) - \mu] dz + \frac{1}{2} \int_{-\infty}^\infty \rho(z) dz \int_{-\infty}^\infty Q(\xi) [\rho(z+\xi) - \rho(z)] d\xi$$

### Curved interface



interfacial energy

$$\mathcal{F} = \int \left\{ \gamma[\rho_0(z)] + \epsilon \bar{\mu} \int_{-\infty}^\infty \rho_0(z) dz \right\} \sqrt{g} d^2 \xi.$$

interface  $x^i(\xi_\alpha)$

tangent  $t^i_\alpha = \frac{\partial x^i}{\partial \xi_\alpha}$

metric  $ds = g_{\alpha\beta} d\xi_\alpha d\xi_\beta$

$g_{\alpha\beta} = t^i_\alpha t^i_\beta$

displace the interface along the normal

$$\delta \sqrt{g} = \frac{1}{2} \sqrt{g} g^{\alpha\beta} \delta g_{\alpha\beta} = \sqrt{g} g^{\alpha\beta} t_\alpha \cdot \delta t_\beta = -(\sqrt{g} g^{\alpha\beta} t_\alpha)_\beta \cdot \mathbf{n} \cdot \delta \mathbf{z}$$

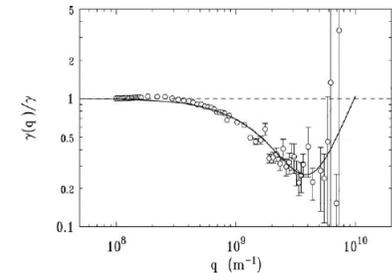
$$= -\sqrt{g} g^{\alpha\beta} \kappa_{\alpha\beta} \delta z.$$

Gibbs-Thomson law

$$(\rho_l - \rho_v) \bar{\mu} - \gamma \kappa = 0$$

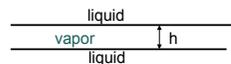
curvature

### Wave-vector-dependent surface energy



Fradin C., Luzet D., Smilgins D., Braslau A., Alba M., Boudet N., Mecke K. and Dailliant J. 2000 *Nature* 403 871

### Interaction of interfaces



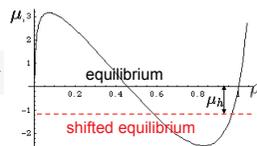
Change of surface tension

$$\gamma_h = \rho_0^+ \int_0^\infty dz \int_{h+z}^\infty Q(\zeta) d\zeta = -\frac{\pi A_l \rho_0^+}{12h^2}$$

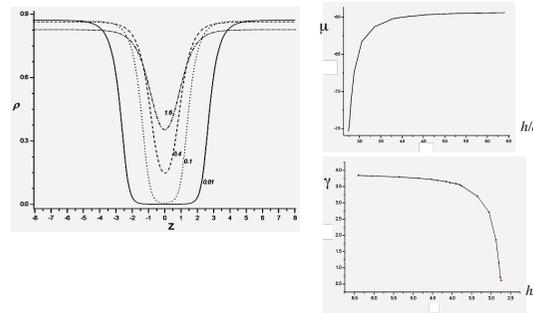
Shift of chemical potential:

$$\mu_h = \int_0^\infty \rho_0^+(z) dz \int_{h+z}^\infty Q(\zeta) d\zeta \approx -\frac{\pi A_l \rho_0^+}{6h^3}$$

...valid at  $h \gg d$   
...significant at  $h \sim d$



### 1d solutions of the nonlocal equations



### Disjoining pressure – nonlocal theory

LP, PRE 64 021603 (2001)

Interaction energy with solid wall

$$F_s = \int \rho(x) dx \int_s U_s(r) \rho_s(x+r) dr$$

$$F = \int_0^\infty \rho(z) [\bar{f}(\rho) + \psi(z) (\alpha_s \rho_s - \frac{1}{2} \rho(z))] dz + \frac{1}{2} \int_0^\infty \rho(z) \int_0^\infty Q(z-\xi) [\rho(\xi) - \rho(z)] d\xi$$

$$\psi(z) = \begin{cases} -\frac{1}{6} \pi A_l z^{-3} & \text{at } |z| > d \\ -\pi A_l d^{-3} \left( \frac{2}{3} - z/2d \right) & \text{at } |z| < d \end{cases}$$

Use profile  $\rho_0(z-h)$ ; compute disjoining pressure  $\Pi = dF/dh$

$$\Pi = \frac{1}{\rho_l - \rho_v} \left\{ \rho_0(-h) \bar{f}(\rho_0(-h)) - \chi \rho_l \int_0^\infty \psi(z) \rho_0'(z-h) dz - \int_0^\infty \psi(z) [\rho_l - \rho_0(-h)] \rho_0'(z-h) dz \right\}$$

sharp interface limit:  $\Pi = -\frac{\pi \chi \rho_l A_l}{6h^3} \frac{H}{6\pi h^3 \rho_l}$  two-term expansion

$$H = \pi^2 \rho_l^2 A_l (\alpha_s \rho_s - \rho_l) \text{ is the Hamaker constant}$$

$$\chi = \alpha_s \rho_s^2 / (\rho_l - 1) \quad \Pi = -\frac{\pi A_l \chi \rho_l}{6h^3} - \frac{\rho_l}{2g'(\rho_l)} \left( \frac{\pi A_l}{6h^3} \right)^2$$

## Disjoining pressure – nonlocal theory

L.P. PRE 64 021603 (2001)

Interaction energy with solid wall

$$F_s = \int \rho(x) dx \int_s U_s(r) \rho_s(x+r) dr$$

$$F = \int_0^\infty \rho(z) \{ \bar{f}(\rho) + \psi(z) [ \alpha_s \rho_s - \frac{1}{2} \rho(z) ] \} dz$$

homogeneous fluid–solid  
+  $\frac{1}{2} \int_0^\infty \rho(z) \int_0^\infty \mathcal{Q}(z-\xi) [ \rho(\xi) - \rho(z) ] d\xi$   
fluid–fluid (distortion)

$$\psi(z) = \begin{cases} -\frac{1}{6} \pi A_s \rho_s^{-3} & \text{at } |z| > d \\ -\pi A_s d^{-3} \left( \frac{2}{3} - z/2d \right) & \text{at } |z| < d \end{cases}$$

interaction kernel

Use profile  $\rho_0(z-h)$ ; compute disjoining pressure  $\Pi = dF/dh$

$$\Pi = \frac{1}{\rho_l - \rho_0} \left\{ \rho_0(-h) \bar{f}(\rho_0(-h)) - \chi \rho_l \int_0^\infty \psi(z) \rho_0(z-h) dz - \int_0^\infty \psi(z) [ \rho_l - \rho_0(-h) ] \rho_0'(z-h) dz \right\}$$

sharp interface limit:  $\Pi = -\frac{\pi \chi \rho_l A_s}{6h^3} = -\frac{H}{6\pi h^3 \rho_l}$

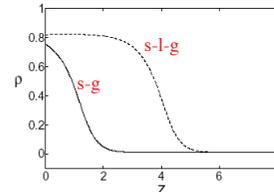
two-term expansion

$$H = \pi^2 \rho_l A_s (\alpha_s \rho_s - \rho_l) \quad \text{is the Hamaker constant} \quad \Pi = -\frac{\pi A_s \chi \rho_l}{6h^3} - \frac{\rho_l}{2g'(\rho_l)} \left( \frac{\pi A_s}{6h^3} \right)^2$$

$$\chi = \alpha_s \rho_s / \rho_l - 1$$

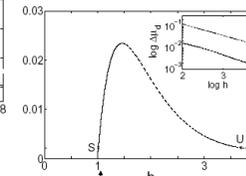
7/23/13

19



Density profile  
(weakly nonwetting fluid)

## Disjoining pressure



$h_f = \text{precursor thickness} \propto \chi^{-1/3}$   
 $\chi = \alpha_s \rho_s / \rho_l - 1$

7/23/13

20

## Local (VdW–GL) theory

assume that density is changing slowly; expand

$$\rho(x+r) = \rho(x) + r \cdot \nabla \rho(x) + \frac{1}{2} r r : \nabla \nabla \rho(x) + \dots$$

retain the lowest order distortion term

$$\mathcal{F} = \int [ \rho \bar{f}(\rho) - \mu \rho + \frac{1}{2} K |\nabla \rho(x)|^2 ] dx \quad K = -\frac{2\pi}{3} \int_d^\infty U(r) r^4 dr$$

Euler – Lagrange equation (van der Waals, 1894)

$$\nabla^2 \rho - g(\rho) + \mu = 0 \quad g(\rho) = d[\rho \bar{f}(\rho)]/d\rho$$

**NB:** divergence in the next order with long-range (VdW) interactions

nonlocal	local
Power tail	Exp. tail

- transition to PDE leads to divergence for long-range forces
- uncertainty in assigning boundary conditions

7/23/13

21

## CUBIC MODEL

Equation for 1d density distribution

$$\rho''(z) - g(\rho) + \mu = 0 \quad g(\rho) = \rho(1-2\rho)(1-\rho)$$

gas–liquid surface tension

$$\gamma = \int_0^1 \rho(1-\rho) d\rho = \frac{1}{6}$$

solid–liquid surface tension

$$\gamma_{sl} = \int_{\rho_s}^1 \rho(1-\rho) d\rho = \frac{1}{6}(1-\rho_s)^2(1+2\rho_s)$$

solid–vapor surface tension

$$\gamma_v = \int_0^{\rho_v} \rho(1-\rho) d\rho = \frac{1}{6}\rho_v^2(3-2\rho_v)$$

Laplace formula

$$\gamma_{sl} - \gamma_{gl} = \gamma \cos \theta$$

$$\rho(0) = \rho_s = 1 - a$$

with  $a \ll 1$

$$\text{yields } \theta = \sqrt{6}a$$

7/23/13

22

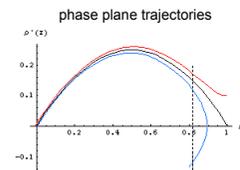
## Density profiles for a weakly non-wetting fluid

$$\rho(0) = \rho_s = 1 - a \text{ with } a \ll 1$$

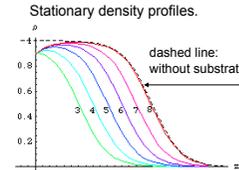
Expand in a  $\rho = \rho_0(z-h) + a \rho_1(z; h) + \dots$

First order  $\rho_1''(z) + g'(\rho_0) \rho_1 = 0, \quad \rho_1'(z) - \rho_1(z) = 0.$

Combined solution  $\rho_a = \rho_0 + a \rho_1 = (1 + e^{2-h})^{-1} - e^{-2}(a - e^{-h})$



7/23/13



23

## Disjoining pressure

Use a solvability condition of the equation for a perturbed profile when the substrate weakly perturbs translational symmetry

$$\mathcal{L} \rho_1 + \mathcal{H}(z) = 0.$$

Inhomogeneity = shift of chemical potential

$$\mathcal{L} = \frac{d^2}{dz^2} + g'(\rho_0)$$

Standard solvability condition:  $\int_{-\infty}^{\infty} \rho_0'(z) \mathcal{H}(z) dz = 0$

solvability condition with boundary terms

$$\int_{z_0}^{\infty} \frac{d\rho_0(z-h)}{dz} \mathcal{H}(z) dz = \left[ \frac{d\rho_0(z-h)}{dz} \frac{d\rho_1(z)}{dz} - \frac{d^2 \rho_0(z-h)}{dz^2} \rho_1(z) \right]_{z=z_0}$$

Compute chemical potential as a function of nominal thickness

$$\Pi(h) \equiv a^2 M(h) = 2a^2 \psi(1-\psi) = 2e^{-h}(a - e^{-h})$$

$$\psi = a^{-1} e^{-h} \ll 1$$

7/23/13

24

## Static profile

$$\gamma h''(x) - \Pi(h) = 0$$

phase plane representation  $h'(x) = p(h)$

$$\frac{\gamma}{2} \frac{d(p^2)}{dh} - \Pi(h) = 0, \quad p(h_f) = 0, \quad p(\infty) = \theta_e$$

static profile (with precursor)

$$p^2 = \frac{2}{\gamma} \int_{h_f}^h \Pi(h) dh = \frac{2}{\gamma} \Phi(h)$$

contact angle

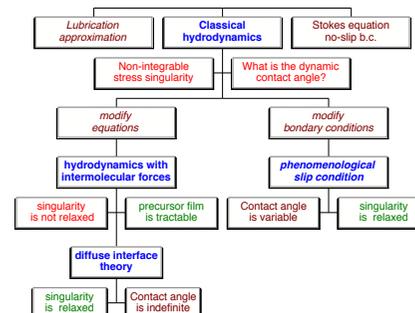
$$\theta_e = \sqrt{\frac{2}{\gamma} [\Phi(\infty) - \Phi(h_f)]} \quad \text{Derjaguin–Frumkin}$$

At  $\theta \ll 1$ ,  $\cos \theta \approx 1 - \frac{1}{2} \theta^2$ , the above result reproduces the standard Young–Laplace formula  $\gamma \cos \theta = \gamma_{gs} - \gamma_{ls}$ . This can be seen by using the relation  $\Pi(h) = d\gamma/dh$  to evaluate the integral explicitly, and observing that  $\gamma(h_f)$  equals to the gas–solid surface tension  $\gamma_{gs}$ , while  $\gamma(\infty) = \gamma + \gamma_{gs}$  is the sum of the gas–liquid and liquid–solid surface tensions.

7/23/13

25

## Contact line: resolving the paradoxes



7/23/13

26

## Conclusions

- Interface is where macroscopic meets microscopic; this is the source of complexity; this is why no easy answers exist
- Motion of a contact line is a *physico-chemical* problem dependent on molecular interaction between the fluid and the substrate
- There is enormous *scale separation* between molecular and hydrodynamic scales, which makes computation difficult but facilitates analytical theory
- Multiscale perturbation theory elucidates dynamics of the contact line, resolves paradoxes, provides tools for the study of various instabilities

7/23/13

27