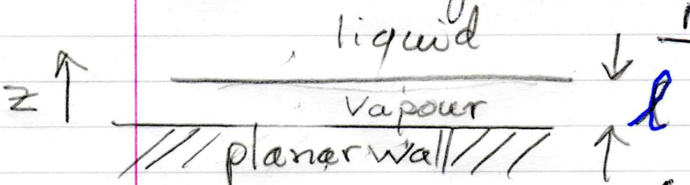
Relating Local Compressibility $\chi(z)$ to Contact Angle θ: Binding Pot.

In a binding pot. treatment we consider the excess grand pot. per unit area $\omega^{ex}(l)$ as a function of a 'film thickness' l.



N.B. l can be defined from Gibbs adsorpt.
Here the Vapour v is intruding between wall w and liquid l
(This is the incipient drying case)

∴ The equilibrium thickness l_{eq} minimizes

$$\omega^{ex}(l) = \underbrace{\gamma_{wv} + \gamma_{lv}}_{\text{surface tensions}} + \omega_B(l) + \delta\mu\,\Delta\rho \qquad (1)$$

$\delta\mu \equiv \mu - \mu_{co}(T)$ and $\delta\mu = 0^+$ at coexistence, i.e. reservoir is a liquid

$\Delta\rho \equiv \rho_l - \rho_v$ is difference in coexisting densities

$\omega_B(l)$ is the binding potential.

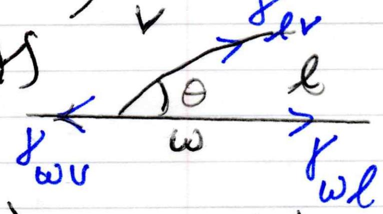
The wall-liquid tension

$$\gamma_{wl} = \omega^{ex}(l_{eq}) \quad ; \quad \delta\mu = 0^+ \qquad (2)$$

$$\therefore \gamma_{wl} = \gamma_{wv} + \gamma_{lv} + \omega_B(l_{eq}) \quad ; \quad \delta\mu = 0^+$$

From Young's equation:

$$\gamma_{wv} - \gamma_{wl} = \gamma_{lv}\cos\theta \qquad (Y)$$



it follows

$$\omega_B(l_{eq}) = -\gamma_{lv}(\cos\theta + 1) \qquad (3)$$

This is a standard result, used in the analysis of surface phase transitions, e.g. R. Evans et. al. JCP **147**, 044701 (2017) Ref. [1], and refs. therein.

[Check: In the approach to drying $\cos\theta \to -1$, $\omega_B(l_{eq}) < 0$.
For wetting, the liquid intrudes and reservoir is a vapour at $\delta\mu = 0^-$. Result corresponding to (3) is $\omega_B(l_{eq}) = \gamma_{lv}(\cos\theta - 1) < 0$.

How $\cos\theta + 1 \to 0$ (drying) depends on the form of $\omega_B(l)$, which depends in turn on the decay of ff and wf potentials.

We can also define a <u>local compressibility</u> via

$$\chi(z) \equiv \left(\frac{\partial \rho(z)}{\partial \mu}\right)_T ,$$

where $\rho(z)$ is the density profile, and choose to approximate

$$\chi(l_{eq}) \simeq -\rho'(z = l_{eq}) \left(\frac{\partial l_{eq}}{\partial \mu}\right)_T \qquad (4)$$

[What will be of interest is the product $\chi(l_{eq})(\cos\theta + 1)$]

Consider <u>SR ff with LR wf</u>

for which critical <u>drying</u> occurs as $\epsilon_w \to 0$

ϵ_w strength of wall-fluid attraction.

Then

$$\omega_B(l) = a e^{-l/\xi_b} + b l^{-2} \qquad (5)$$

ξ_b bulk correl length of V; intruding phase

$$a > 0 \quad \text{and} \quad b = -\Delta\rho\, \epsilon_w \epsilon_{LJ} \sigma^3/2 < 0 \qquad (6)$$

see [1]. σ = LJ diameter, ϵ_{LJ} = LJ well-depth.

Requiring

$$\left.\frac{\partial \omega^{ex}}{\partial l}\right|_{l_{eq}} = 0$$

yields

$$\frac{a}{\xi_b} e^{-l_{eq}/\xi_b} = -2b\, l_{eq}^{-3} \quad , \delta\mu = 0^+ \qquad (7)$$

and Eq (30) of Ref [1] which was tested in [1], for small ϵ_w, using DFT.

The local compressibility is easily calculated:

$$\left(\frac{\partial l_{eq}}{\partial \mu}\right)_T = -\Delta\rho \left(\frac{a}{\xi_b^2} e^{-l_{eq}/\xi_b} + \frac{6b}{l_{eq}^4}\right)^{-1} = -\Delta\rho \left(\frac{a}{\xi_b^2} e^{-l_{eq}/\xi_b} - \frac{3a e^{-l_{eq}/\xi_b}}{\xi_b l_{eq}}\right)^{-1} , \delta\mu = 0^+ \qquad (8)$$

augments Eq (32) of [1]. To obtain the contact angle θ we use (3).

Substituting (7) into (5) we find

$$\omega_B(l_{eq}) = a e^{-l_{eq}/\xi_b} - \frac{a}{2\xi_b} l_{eq} e^{-l_{eq}/\xi_b}$$

$$= a e^{-l_{eq}/\xi_b} \left[1 - l_{eq}/2\xi_b\right] \qquad (9)$$

Check: In the approach to (critical) drying $\epsilon_w \to 0$, 2nd term in (9) >> 1st and $\omega^{ex}(l_{eq}) < 0$.

Using Eq (30) of [1] (see next pg.)

$$\omega_B(l_{eq}) \approx a\, \epsilon_w \left(\frac{l_{eq}}{\xi_b}\right)^{-3} \left(\frac{-1}{2}\right) \left(\frac{l_{eq}}{\xi_b}\right)$$

2

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Using Eq (30) of [1] (see next pg.)

$$\omega_B(l_{eq}) \simeq a\, \epsilon_w \left(\frac{l_{eq}}{\xi_b}\right)^{-3} \left(\frac{-1}{2}\right)\left(\frac{l_{eq}}{\xi_b}\right)$$

$$-l_{eq}/\xi_b = \ln\epsilon_\omega - 3\ln(l_{eq}/\xi_b) + \text{const.} \qquad \text{(30) of [1]}$$

It follows that

$$\omega_B(l_{eq}) \approx -\frac{a}{2}\epsilon_\omega\left(\frac{l_{eq}}{\xi_b}\right)^{-2} \approx -\frac{a}{2}\epsilon_\omega(-\ln\epsilon_\omega)^{-2}$$

so from (3)

$$(\cos\theta+1)\gamma_{lv} \approx \frac{a}{2}\epsilon_\omega(-\ln\epsilon_\omega)^{-2}, \quad \epsilon_\omega\to 0$$

This has correct dimensions and is (36) of [1].

We attempt to combine (8) and (9)

$$\omega_B(l_{eq})\cdot\left(\frac{\partial l_{eq}}{\partial\mu}\right)_T = a e^{-l_{eq}/\xi_b}[1-l_{eq}/2\xi_b]\cdot\left(-\Delta\rho\left[\frac{a e^{-l/\xi_b}}{\xi_b}\right]^{-1}\right)\left(\frac{1}{\xi_b}-\frac{3}{l_{eq}}\right)^{-1}$$

$$= -\Delta\rho\,\xi_b[1-l_{eq}/2\xi_b]\Big/\left(\frac{1}{\xi_b}-\frac{3}{l_{eq}}\right)$$

$$= -\Delta\rho[1-l_{eq}/2\xi_b]\xi_b^2/(1-3\xi_b/l_{eq}) \qquad (10)$$

{Has correct dimension} ↳ dominates near drying

Check: in approach to drying $\epsilon_\omega\to 0$, this product must vary as l.h.s. $\epsilon_\omega(-\ln\epsilon_\omega)^{-2}\cdot\epsilon_\omega^{-1}(-\ln\epsilon_\omega)^{3} = (-\ln\epsilon_\omega)$ ✓
but r.h.s. $\sim l_{eq} \sim (-\ln\epsilon_\omega)$ ∴ OK.

Translate (10) to contact angle using (3):

$$-\gamma_{lv}(\cos\theta+1)(\partial l_{eq}/\partial\mu)_T = \xi_b^2\Delta\rho[1-l_{eq}/2\xi_b]/(1-3\xi_b/l_{eq})$$

$$= -\xi_b^2\Delta\rho\left[1-\frac{l_{eq}}{2\xi_b}\right]\left[1+\frac{3\xi_b}{l_{eq}}+\frac{9\xi_b^2}{l_{eq}^2}+\dots\right]$$

(Assuming $3\xi_b/l_{eq} < 1$)

$$= -\xi_b^2\Delta\rho\left[-\frac{l_{eq}}{2\xi_b}+1+\frac{3\xi_b}{l_{eq}}-\frac{3}{2}+\frac{9\xi_b^2}{l_{eq}^2}-\frac{9}{2}\frac{\xi_b}{l_{eq}}\right]$$

$$\therefore\ \gamma_{lv}(\cos\theta+1)\left(\frac{\partial l_{eq}}{\partial\mu}\right)_T = \xi_b^2\Delta\rho\left[-\frac{l_{eq}}{2\xi_b}-\frac{1}{2}-\frac{3}{2}\frac{\xi_b}{l_{eq}}+O\left((\xi_b/l_{eq})^2\right)\right] \qquad (11)$$

{Has correct sign near drying: $(\partial l_{eq}/\partial\mu)_T<0$} $[\ ] = A$

We now use (4) to introduce $\chi(l_{eq})$:

4

$$\gamma_{lv}(\cos\theta+1)\chi(l_{eq}) = -\rho'(l_{eq})\,\xi_b^2\,\Delta\rho\,[A] \qquad (12)$$

where ξ_b refers to ξ_v / vapour for drying

Recall: in BULK: $\chi_b = (\partial\rho_b/\partial\mu)_T = \rho_b^2\,\kappa_T$

usual isothermal compressibity

Eq. (12) suggests we reconsider the formula for the lv surface tension given in Parry et. al. (2016)

Here we have

$$\gamma_{lv} = \frac{f_2\,(\Delta\rho)^2}{3(\xi_l+\xi_v)} \qquad (13)$$

(their (85)) liquid, vapour bulk correl. length

This follows from a square-gradient DFT.

- Notation Parry: $\sigma \equiv \gamma_{lv}$ = liquid-vapour tension in the DFT

f_2 is the coeff. of the sq. gradient term and is assumed to be constant.

If we choose to focus on the bulk liquid compressibity then

bulk correl. length: $\xi_l^2 = f_2/\phi''(\rho_l)$.

And $\chi_b^l = [\phi''(\rho_l)]^{-1}$, refers to liquid.

Here $\phi(\rho)$ is the bulk free energy density.

Thus the bulk liquid correlation length: $\xi_l^2 = f_2\,\chi_b^l \qquad (14)$

see also B. Q. Lu et. al (1985) below.

It follows that from (13): $\gamma_{lv} = \xi_l^2/\chi_b^l \cdot \dfrac{(\Delta\rho)^2}{3(\xi_l+\xi_v)}$

where we choose to focus on the bulk liquid compressibility.

Now substitute into (12):

$$(\cos\theta+1)\,\xi_l^2\,\frac{\chi(l_{eq})}{\chi_b^l}\,\frac{(\Delta\rho)^2}{3(\xi_l+\xi_v)} = -\rho'(l_{eq})\,\xi_b^2\,\Delta\rho\cdot[A]$$

Recall: in the case of drying: $\xi_b = \xi_v$: the vapour is intruding.

$$\therefore\ (\cos\theta+1)\frac{\chi(l_{eq})}{\chi_b^l} = -\frac{\rho'(l_{eq})}{\Delta\rho}\,3(\xi_l+\xi_v)\left(\frac{\xi_v}{\xi_l}\right)^2[A] \qquad (15)$$

[Check: Dimension OKAY]

We might suppose: $\rho'(l_{eq}) \simeq \Delta\rho / w$

measure of width of 'interface'

Then (15) reduces to:

$$(\cos\theta+1)\frac{\chi(l_{eq})}{\chi_b^l} = -\frac{3}{w}(\xi_l+\xi_v)\left(\frac{\xi_v}{\xi_l}\right)^2[A]$$

−ve.

$$= -\frac{3}{w}\xi_l\left(1+\frac{\xi_v}{\xi_l}\right)\left(\frac{\xi_v}{\xi_l}\right)^2\left[-\frac{l_{eq}}{2\xi_v}-\frac{1}{2}-\frac{3}{2}\frac{\xi_v}{l_{eq}}+H.O.\right] \quad (16)$$

is +ve. ✓

<u>Estimates</u>†: $\xi_v/\xi_l \sim 0.42$ at $T/T_c = 0.7$

$$(\cos\theta+1)\frac{\chi(l_{eq})}{\chi_b^l} = +3(1.42)0.42^2\,\frac{l_{eq}/w}{2\times 0.42}$$

at leading order

$$= 0.89\,\frac{l_{eq}}{w}. \quad (17)$$

† B.Q. Lu, R. Evans and M.M. Telo da Gama Molec. Phys. <u>55</u>, 1319, (1985)

See Figs. 3, 4.

<u>Note</u>: these refer to <u>bulk</u> correlation lengths from a square gradient theory. More sophisticated approaches will yield somewhat different ratios.

† The same paper indicates (Fig. 10) that the width of the free l.v. interface $w \approx 2.5\sigma_{LJ}$ for $T/T_c = 0.7$.

$\boxed{\text{Remarks:}}$

i) The analysis presented is for large contact angle $\theta > \pi/2$ and should be 'exact' in the limit of critical drying: $(\cos\theta+1) \to 0^+$, when ff is SR and wf is LR. This case is the easiest to analyse since we know critical drying occurs as $\epsilon_w \to 0$.

ii) How general might the conclusion be? We should consider other binding potentials that lead to other types of drying or wetting transitions. In particular we need to understand a 1st order wetting transition. What does the product $(1-\cos\theta)\chi(l_{eq})$ look like in this situation?

iii) How far can one trust a formula such as (17)

when one is not very close to drying, i.e. when ε_w is substantial and $\cos\theta$ is substantially > -1.
In these circumstances l_{eq} is small, $\sim \sigma_{LJ}$, the fluid-fluid diameter.
The work of Many Coe suggests that binding potential predictions work down to surprisingly small length scales – so there is hope that these might provide insight outside the critical drying regime.

iv) Eq (17) has an interesting structure. On l.h.s. $\cos\theta = (\gamma_{wv} - \gamma_{wl})/\gamma_{lv}$ is clearly determined by macroscopic quantities. χ^l is clearly the (macroscopic) bulk 'compressibility'. $\chi(l_{eq})$ is a 'local quantity'.
On the r.h.s. we have interfacial quantities pertaining to a near-drying situation.
Obviously, within DFT / or simulations one could calculate $\rho'(l_{eq})$. And l_{eq} is is defined via the Gibbs adsorption: $\Gamma = \int_0 dz\,(\rho(z) - \rho_b) \equiv -\Delta\rho\, l_{eq}$, for drying.
The r.h.s. is a mixture of macroscopic (integrated) quantities Γ and a local measure w.

v) Clearly one might test (16) or (17) within DFT or simulation, especially away from critical drying. What might one learn?

Bob (25/10/22).

N.B. a) I should check out paper by J.R. Henderson where I think he showed how to generate a (perfectly) flat density profile at a wall.
b) When we consider the binding potential $\omega_B(l)$ I am reminded of the work (simulation) by J.R. Errington. We should look at this.