Product $\chi_T \sigma$ near T_c

χ_T: bulk compressibility; σ: liquid-vapour surface tension

See e.g. A.O. Parry et. al. JPCM, 28, 244013 (2016) for pertinent formulae.

For simple square-gradient approx.

$$\mathcal{F}_v[\rho] = \int d\underset{\sim}{r} \left\{ \underbrace{\frac{f_2}{2}}_{\text{take const in MF}} (\nabla\rho)^2 + \underbrace{\phi(\rho)}_{\text{Double well: giving coexistence of 2 phases.}} \right\}$$

Curvatures $\phi''(\rho_g)/f_2 = \kappa_g^2$ $\qquad \phi''(\rho_\ell)/f_2 = \kappa_\ell^2$

where for bulk (b) $\kappa_g = \xi_g^{-1}$ and $\kappa_\ell = \xi_\ell^{-1}$, denote (inverse) bulk correlation lengths of gas (g) and liquid (l)

Bulk structure factor:

$$S_b(k) = S(0)/(1 + k^2\xi_b^2)$$

with $S(0) \propto$ compressibility χ_T

Tension:
$$\sigma = f_2 \int_{-\infty}^{\infty} dz\, \rho'(z)^2 = \int_{\rho_g}^{\rho_\ell} d\rho \sqrt{2 f_2 (\phi(\rho) - \phi(\rho_g))}$$

In the JPCM a double quartic potential is considered. (Sec. 3.2). This yields tanh density profiles and a surface tension:

$$\sigma = \frac{f_2 (\Delta\rho)^2}{3(\xi_\ell + \xi_g)} \qquad (85)$$

with $\Delta\rho = \rho_\ell - \rho_g$, diff. in coexisting densities

Check: dimensions are correct. $f_2 : [E L^5]$ $\quad \sigma : [E L^{-2}]$.

How does this behave close to bulk T_c?

a) MF. $\quad f_2 = \text{const.}$ $\quad \Delta\rho \sim t^{+1/2}$; $\quad \xi_b \sim t^{-1/2}$, $t \to 0$

with $t = (T_c - T)/T_c$

$\therefore \sigma \sim t^{3/2}$ — the standard MF result

And, of course, the bulk compressibility $\chi_T \sim t^{-1}$

It follows that the product

$$\sigma \chi_T \sim t^{1/2}, \quad t \to 0$$

i.e. it vanishes, and is consistent with MF exponents, for σ and χ_T.

b) Beyond M F.

Now caution is required.

a) Suppose we simply begin with the product $\sigma \chi_T$.

We Know $\sigma \sim t^{(d-1)\nu}$ from hyperscaling

Thus in dim. $d = 3$ $\sigma \sim t^{2\nu}$

where $\xi_b \sim t^{-\nu}$, $t \to 0$

And $\chi_T \sim t^{-\gamma}$.

Use the Fisher scaling relation: $\gamma = (2-\eta)\nu$

Then the product

$$\chi_T \sigma \sim t^{-\gamma} t^{(d-1)\nu} \sim t^{2\nu - \gamma} \sim t^{\eta\nu}$$

which vanishes for $d=3$: but slowly:

$\eta \sim 0{\cdot}03$ is small in $d=3$. and $\nu \simeq 0{\cdot}63$

b) Now start with (85). This would arise from a Fisk-Widom treatment:

$$\sigma \sim \underbrace{t^{-\eta\nu}}_{\xi_2} \, t^{2\beta} \, t^{\nu}$$

ξ_2 actually diverges beyond MF: but slowly.

The product $\chi_T \sigma$ is then

$$\chi_T \sigma \sim t^{-\gamma - \eta\nu + 2\beta + \nu} \quad \text{(usual exponents)}$$

but $2\beta + \gamma = 2 - \alpha$ (Rushbrooke equality)

$$\therefore \chi_T \sigma \sim t^{-\gamma - \eta\nu + 2 - \alpha - \gamma + \nu}$$

Now use: $\gamma = (2-\eta)\nu$ (Fisher) and $2 - \alpha = d\nu$

$$\chi_T \sigma \sim t^{-2\gamma - \eta\nu + d\nu + \nu}$$

$$\sim t^{-2(2-\eta)\nu - \eta\nu + d\nu + \nu}$$

$$= t^{\eta\nu} \quad (d=3)$$

as given in a), i.e. we recover the general scaling result, as expected.

c) Return to formula (85) and result for χ_T within same theory (Double quartic).
The bulk compressibility is
$$\chi_T = \rho^{-2}(\partial\rho/\partial\mu)_T = \rho^{-2}[\phi''(\rho)]^{-1}$$
in the present analysis.
Thus the product
$$\chi_T\sigma = \frac{1}{\rho^2\,\phi''(\rho)} \cdot \frac{f_2(\Delta\rho)^2}{3(\xi_\ell+\xi_g)}$$
Check dimension: $[EL^5]/[EL^3.L] = [L]$

Assume χ_T refers to the bulk liquid then
$$\phi''(\rho_\ell)/f_2 = \kappa_\ell^2$$
And at low T, near triple point, $\Delta\rho = \rho_\ell - \rho_g \simeq \rho_\ell$
Then
$$\chi_T^\ell\sigma \simeq \frac{1}{\kappa_\ell^2\, 3(\xi_\ell+\xi_g)}$$
$$= \xi_\ell^2 / 3(\xi_\ell+\xi_g)$$
$$= \frac{\xi_\ell}{3}/(1+\xi_g/\xi_\ell)$$

Typically $\xi_g/\xi_\ell \sim 1/2$ at low T. Thus
$$\chi_T^\ell\sigma \simeq \xi_\ell/4{\cdot}5.$$
A typical value of ξ_ℓ for an argon type fluid near the triple point is $\xi_\ell \sim 0{\cdot}6D$ → molec. diameter

It follows that $\chi_T^\ell\sigma \simeq 0{\cdot}13D$ (A)
which is fairly close to previous estimates.
The upshot is that, at low T, the product $\chi_T^\ell\sigma$ should be roughly constant and about $0{\cdot}1 *$ fluid diameter [This seems to be borne out by exp. results]

- Physics of (A). Sq. Gradient theory + Double Quartic Pot. should capture key features. (A) is very much a result pertaining to the bulk compressibility χ^ℓ.
- The larger is the tension (stiffer interface) the more likely is the compressibility to be small.