Molecular simulation of nano-dispersed fluid phases

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Stable and unstable phase equilibria

Equilibrium condition for a droplet containing $j$ molecules:

$$p = p(T, j)$$

$\Delta G$ at constant $p$ and $T$:

1 unstable equilibrium

$\Delta F$ at constant $V$ and $T$:

(1 unstable equilibrium)

1 stable equilibrium
Intervention rate and nucleation rate

Not all of the removed clusters would have grown to macroscopic size

\[ J = J_\theta q(\theta). \]

The probability for a droplet to grow from size \( \theta \) to infinity is

\[ q(\theta) = \frac{\int_1^\theta dn \exp\left(\frac{2F}{T}\right)}{\int_1^\infty dn \exp\left(\frac{2F}{T}\right)}, \]

and for the critical nucleus it is approximately \( q(n^*) \approx 1/2 \).
Nucleation rates from molecular simulation

CNT overstates activation energy, but the slope of $J$ (critical size) is correct.
Equilibrium vapour pressure of a droplet

Canonical MD simulation of LJTS droplets

- Vrabec et al. (2006)
- Horsch et al. (2008)
- Napari et al. (2009)
- Capillarity, i.e. CNT

Down to 100 molecules: agreement with CNT ($\gamma = \gamma_0$).

At the spinodal, the results suggest that $R_{\gamma} = 2\gamma / \Delta p \to 0$.

This implies

$$\lim_{R_{\gamma} \to 0} \gamma = 0,$$

as conjectured by Tolman (1949) …
Extrapolation to the planar limit

• The deviation between the equimolar radius and the capillarity radius is consistently found to be smaller than $\sigma/2$.

• The curvature dependence of $\gamma$ is weak: The deviation from the planar surface tension is smaller than 10\% for radii larger than $5\sigma$ (about 2 nm).

Radial parity plot

$\delta_0 = \lim_{\Delta p \to 0} (R_\kappa - R_\rho)$

LJTS fluid
- $R_\kappa$ from IK
- $R_\kappa$ from $\rho$

$T = 0.75\ \varepsilon$
$T = 0.85\ \varepsilon$
Interpolation to the planar limit

- Convention: Negative curvature (bubbles), positive curvature (droplets).

- Properties of the planar interface, such as its Tolman length, can be obtained by interpolation to zero curvature.

- A positive slope of $\Delta p/2R_\rho$ over $1/R_\rho$ in the Nijmeijer diagram corresponds to a negative $\delta$, on the order of $-0.1\,\sigma$ here, conforming that $\delta$ is small.

- However, $R \to 0$ for droplets in the spinodal limit for the surrounding vapour (Napari et al.) implies $y \to 0$. 
Simulation of thin planar liquid films

By simulating thin liquid films, curvature-independent size effects can be considered.

As expected, the density in the centre of nanoscopic liquid slabs deviates significantly from that of the bulk liquid at saturation.
Curvature-independent size effect

Surface tension for thin slabs:

Relation with $\gamma(R)$ for droplets?

$\delta_0$ is small and probably negative

Malijevský & Jackson (2012):

$\delta_0 = -0.07$

"an additional curvature dependence of the $1/R^3$ form is required …”

Correlation: $\frac{\gamma(d, T)}{\gamma_0(T)} = 1 - \frac{b(T)}{d^3}$
Conclusion

• The vapour pressure of a nanodroplet is supersaturated due to curvature. Its equilibrium properties are related to its role as a critical nucleus for the condensation of a metastable supersaturated vapour.

• These effects are well described by the capillarity approximation and classical nucleation theory, down to droplets containing 100 molecules. Very high supersaturations, however, correspond to extremely small droplets, implying a decrease in the surface tension.

• An approach based on effective radii which can be rigorously determined by simulation proves the Tolman length to be small. For extremely small dispersed phases, the surface tension is reduced due to a curvature-independent effect which is also present for planar films.