Physics of Liquid Matter: Modern Problems, 5th International Conference

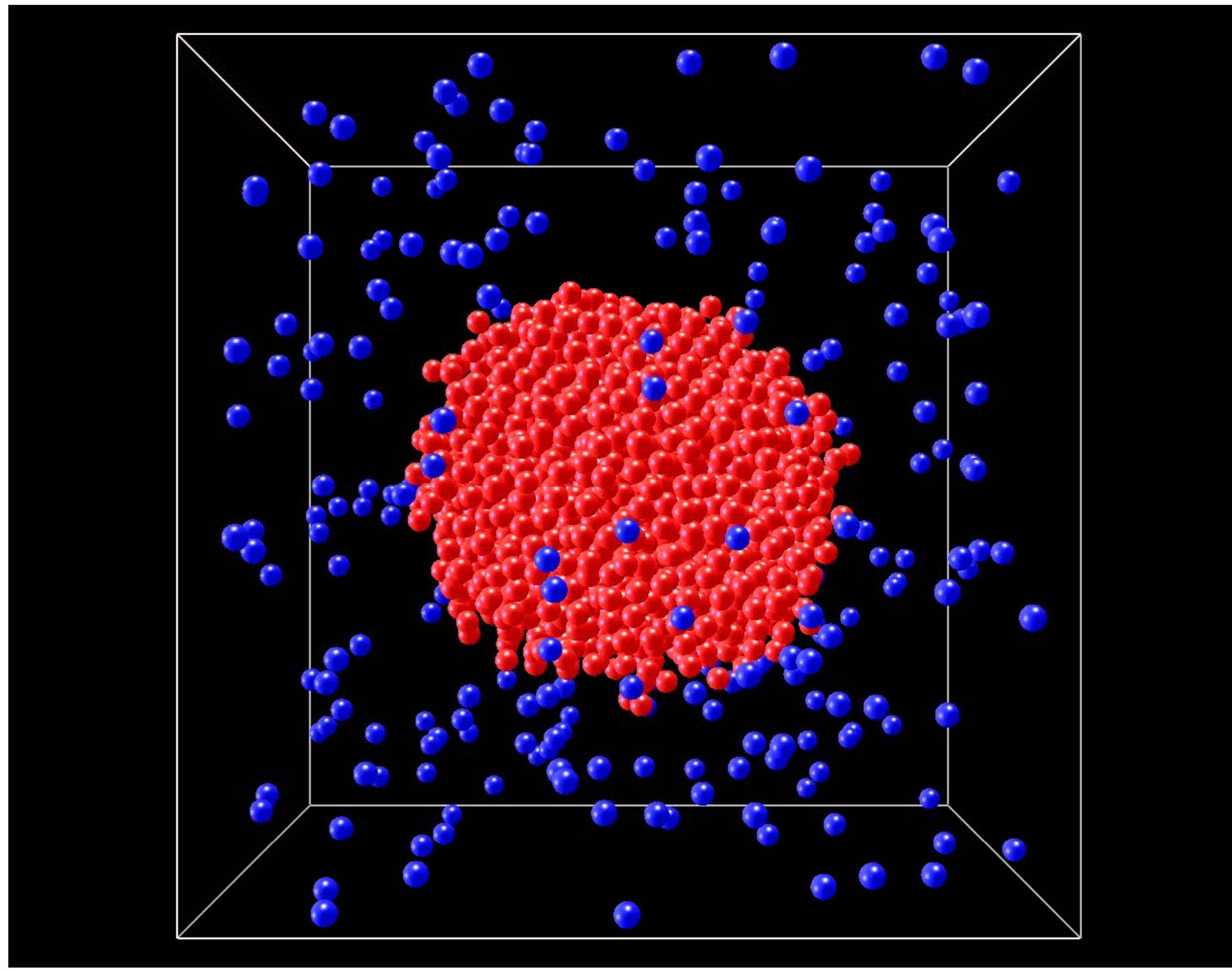
The curved vapor-liquid interface of the Lennard-Jones fluid

Taras Shevchenko Kyiv National University, May 23, 2010

M. Horsch, S. Miroshnichenko, S. Olma, Z. Wei, A. Zibart, and J. Vrabec

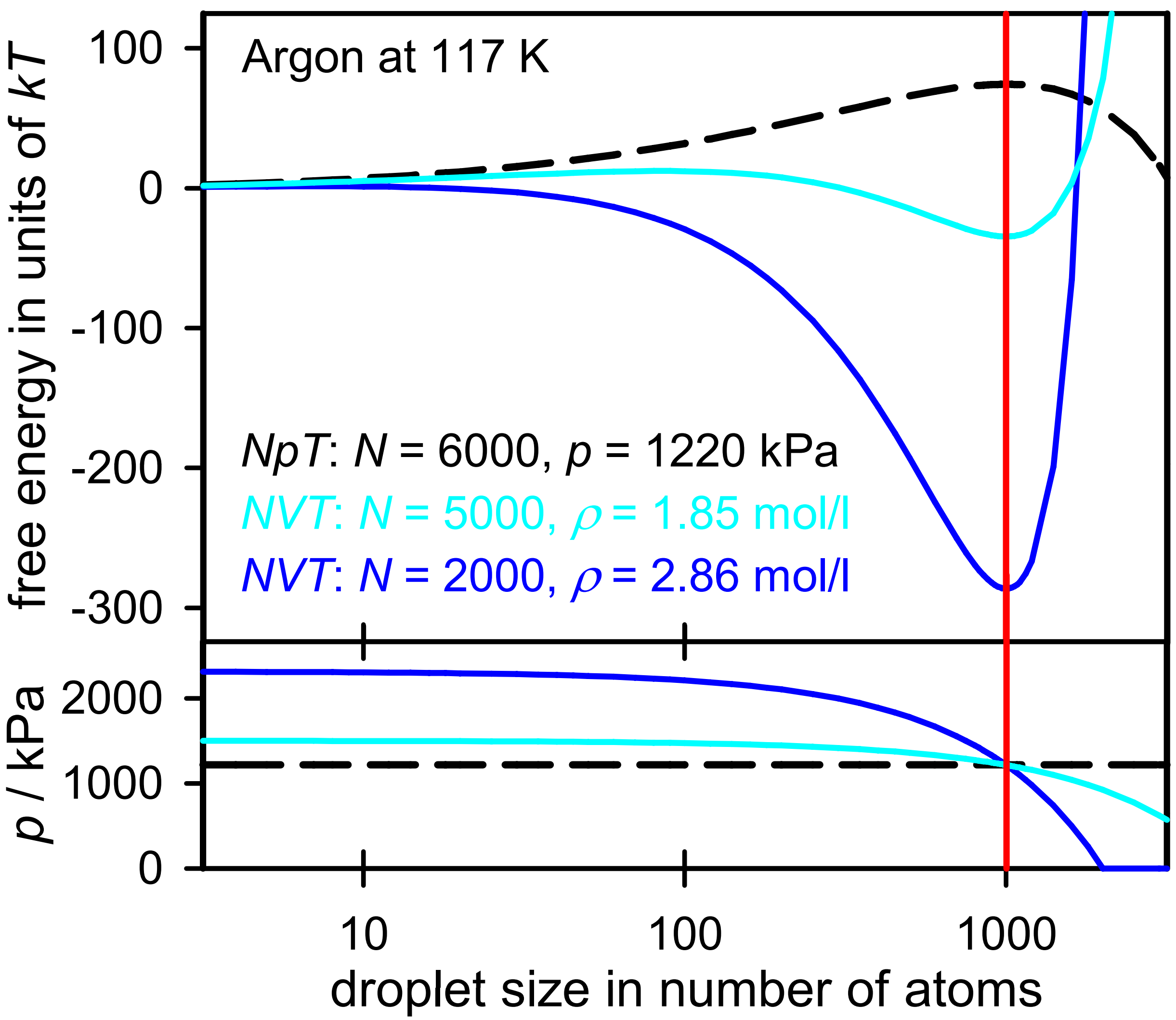
MD simulation of a single droplet

- Vapor and liquid are equilibrated separately
- A small (n < 10000) droplet is inserted into the vapor
- If the droplet cannot evaporate completely, an equilibrium is established within a few nanoseconds



truncated-shifted LJ fluid ($r_c = 2.5\sigma$)

Equilibrium vapor pressure



Equilibrium condition for a droplet containing n atoms:

$$p = p(T, n)$$

ΔG at constant p and T:

1 unstable equilibrium

ΔF at constant V and T:

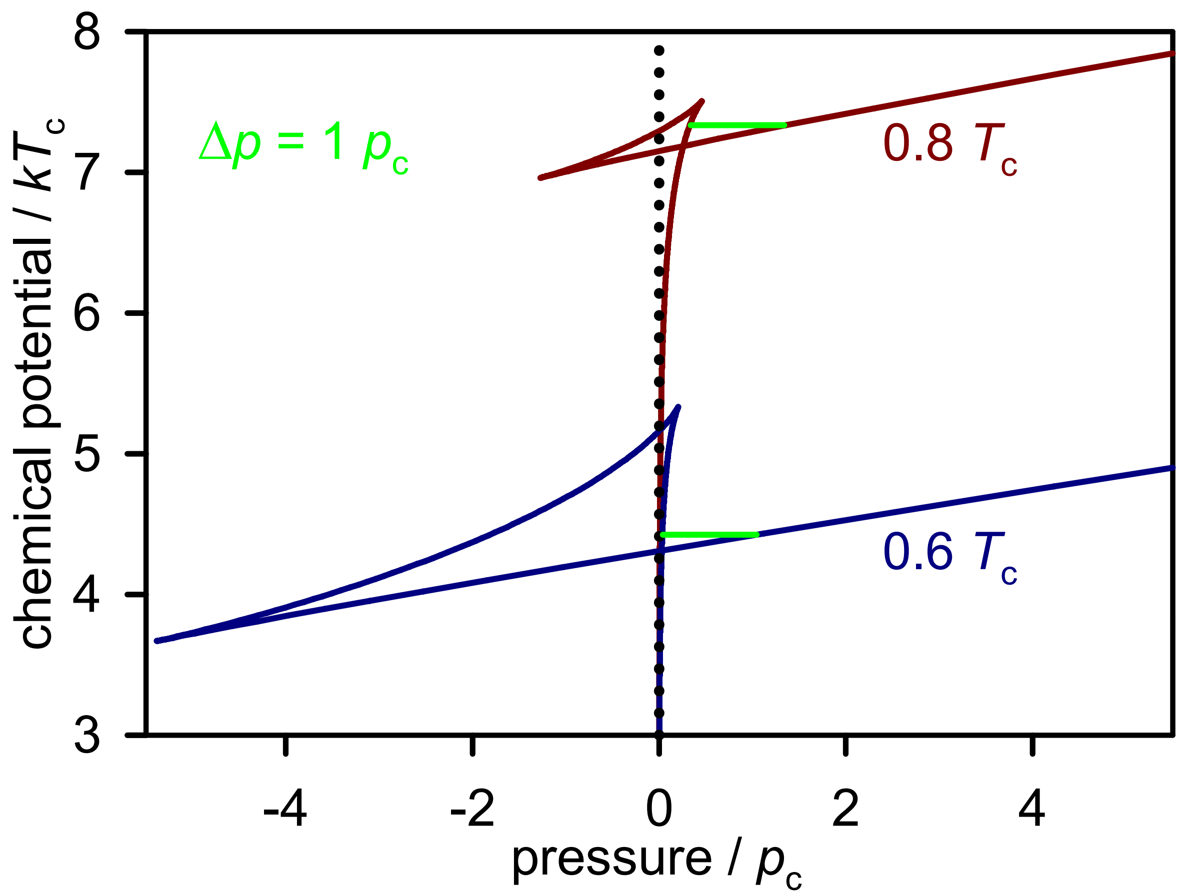
1 unstable equilibrium

1 stable equilibrium

Convex spherical interfaces in equilibrium

$$p_\ell - p_\mathrm{v} = \frac{2\gamma}{R_\mathrm{L}}$$

Interpretation: Definition of the Laplace radius R_L

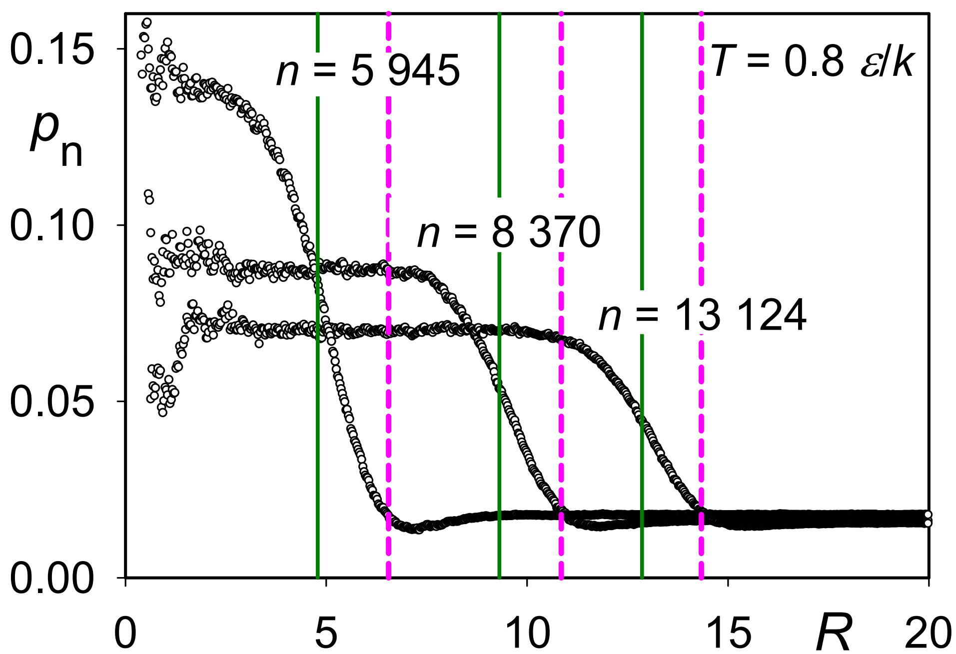


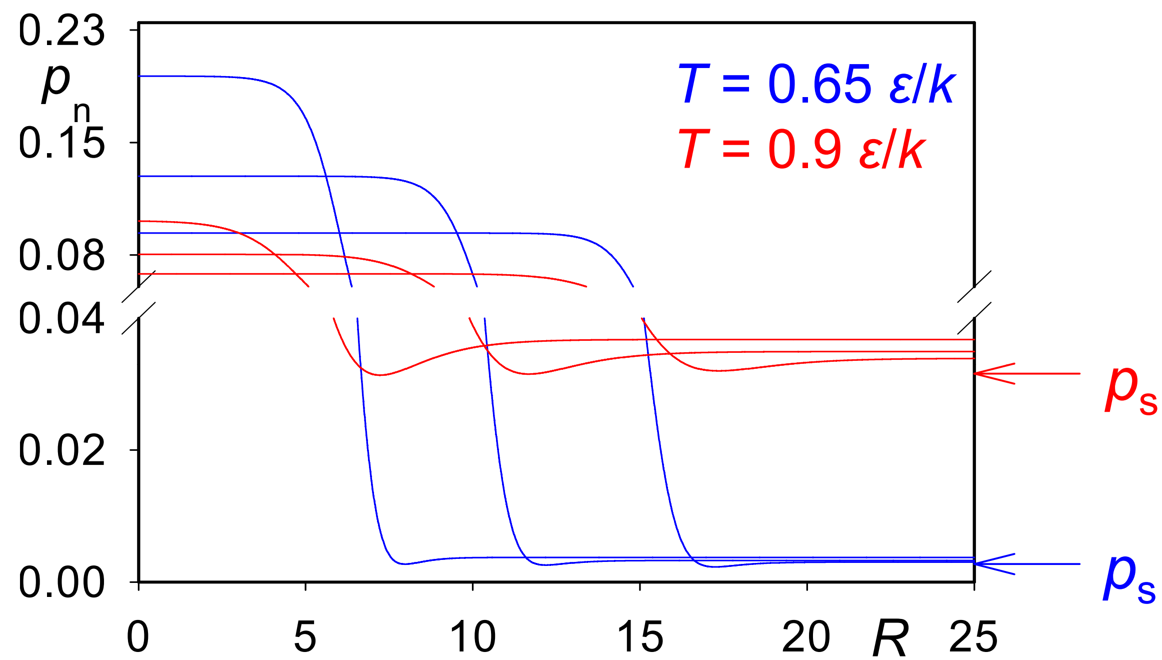
Droplet / positive curvature

Supersaturated fluid phases

Normal pressure profile

From the average Irving-Kirkwood pressure tensor in polar coordinates:



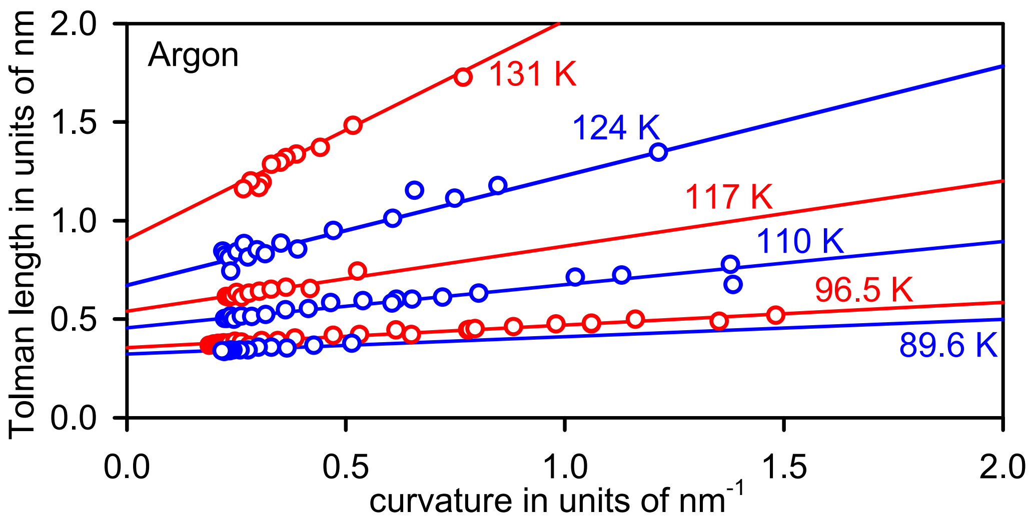


- - - Equimolar radius R_e

—— Laplace radius R_L

$$p_v - 2p_n(R) + p_\ell = (p_0 - p_v)\tanh\left(2D_v^{-1}[R - R_v]\right) + (p_\ell - p_0)\tanh\left(2D_\ell^{-1}[R - R_\ell]\right)$$

Droplet surface tension



For small droplets, the Tolman length

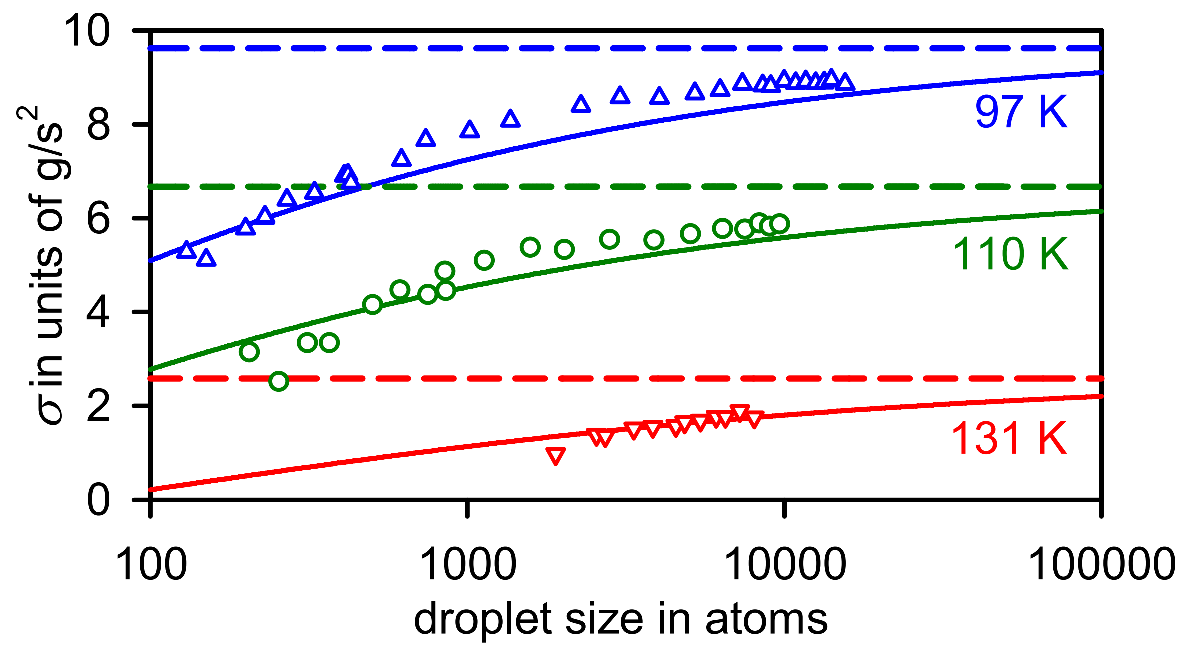
$$\delta = R_e - R_L$$

is significantly elevated.

Tolman equation:

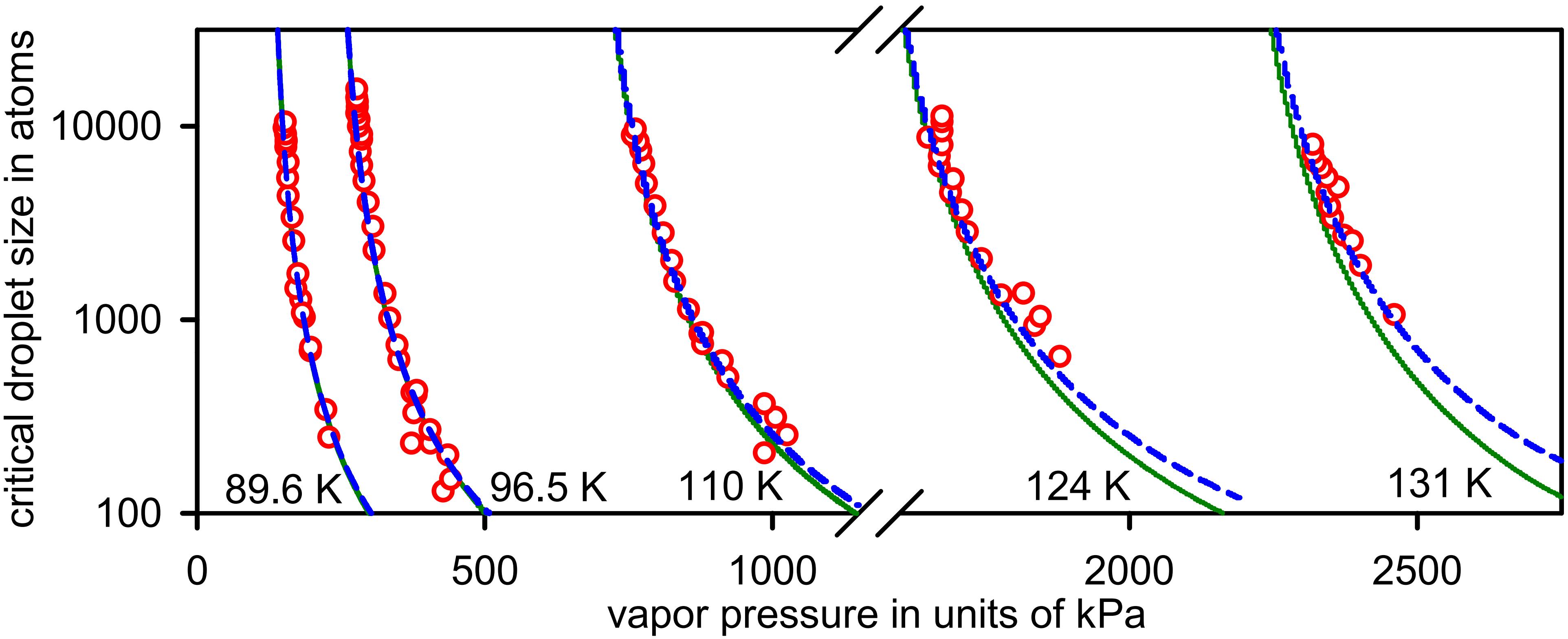
$$\frac{\gamma_\infty}{\gamma_0} \approx \frac{R_e + \delta_\infty}{R_e - \delta_\infty}$$

- ● simulation
- — Tolman equation
- - - - planar interface



Single droplet in equilibrium

Argon (truncated-shifted LJ model)



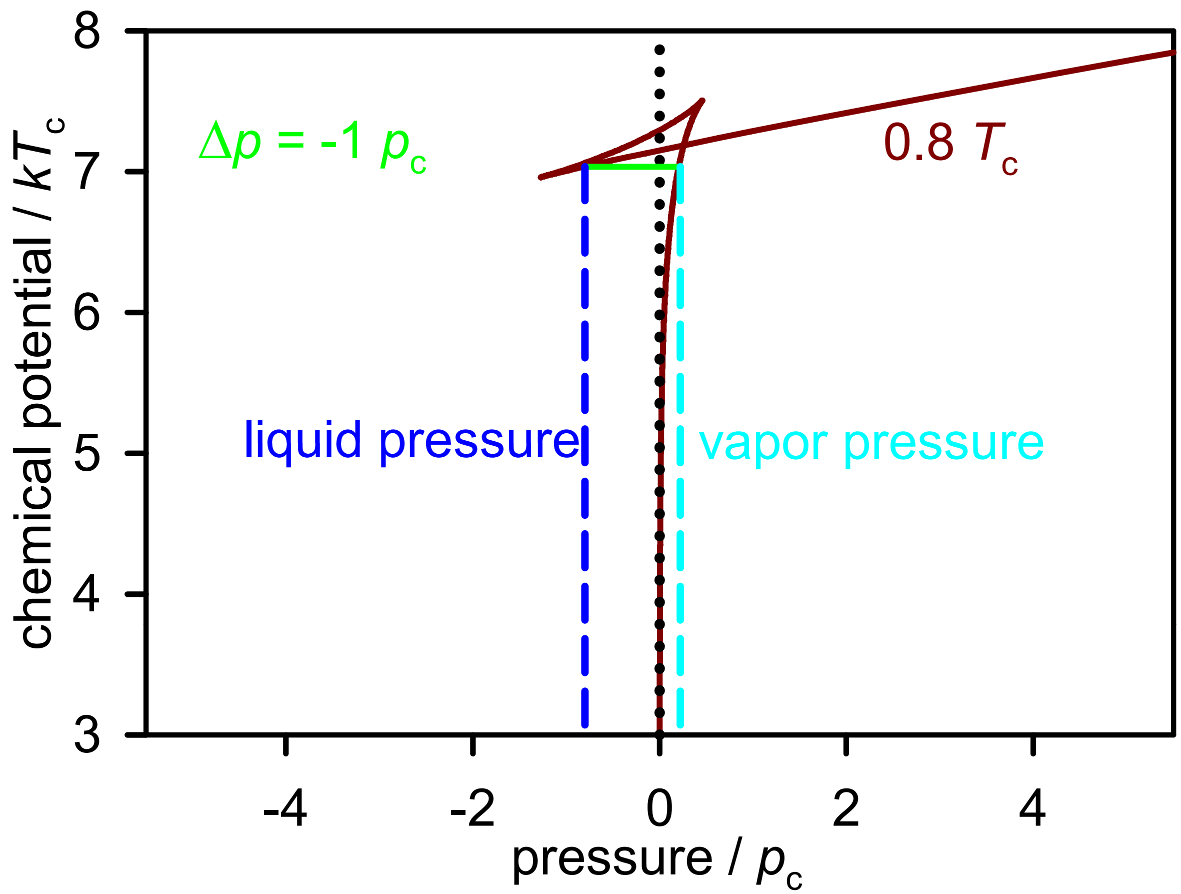
"standard" CNT $n^* = \left(\frac{2\gamma_0 a}{3(\mu - \mu_s)} \right)^3$

CNT with the pressure effect $n^* = \left(\frac{2\gamma_0 a}{3\Delta\mu_{eff}} \right)^3$

Concave spherical interfaces in equilibrium

$$p_\ell - p_\mathrm{v} = \frac{2\gamma}{R_\mathrm{L}}$$

Interpretation: The Laplace radius R_L is negative.



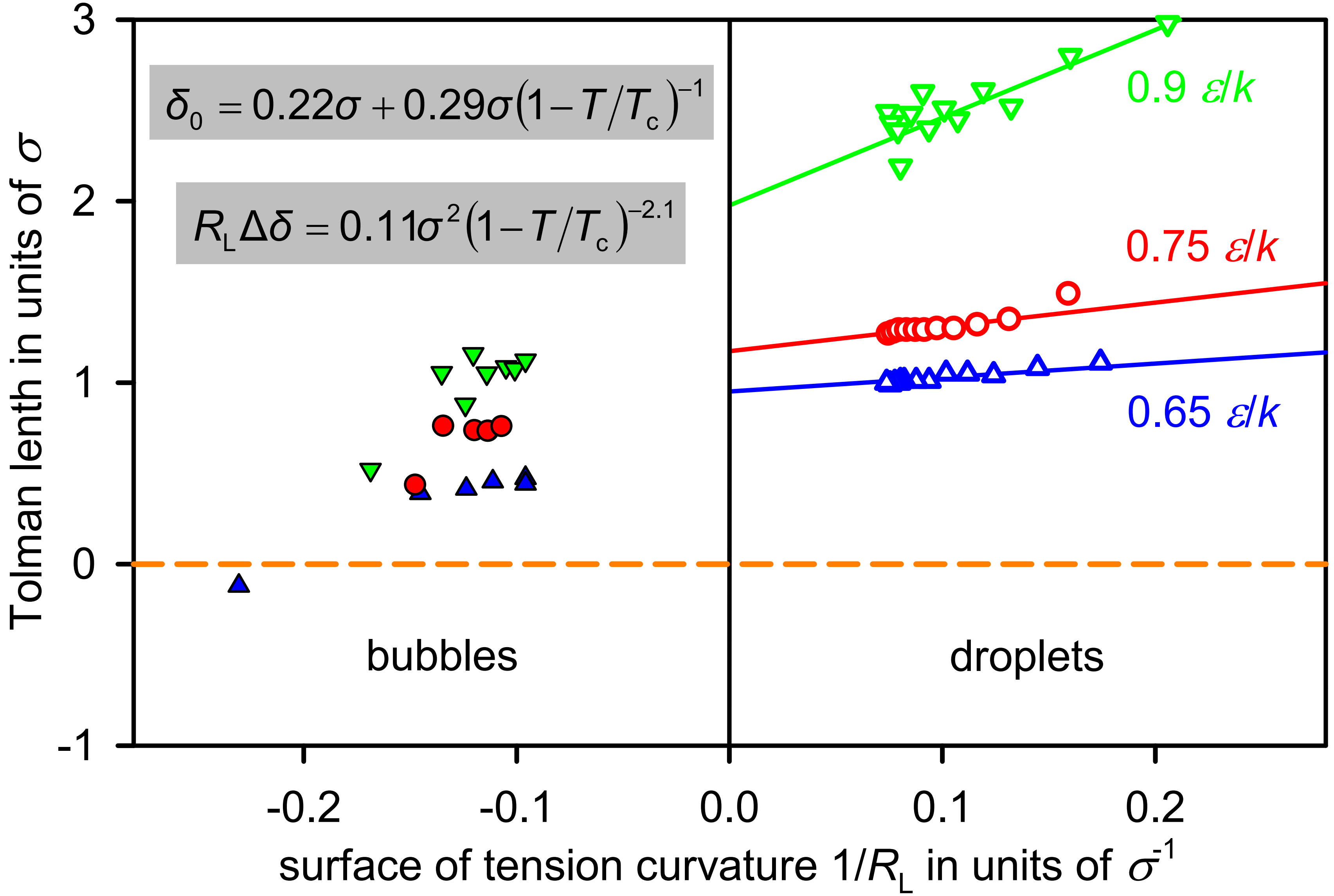
Droplet / positive curvature

Supersaturated fluid phases

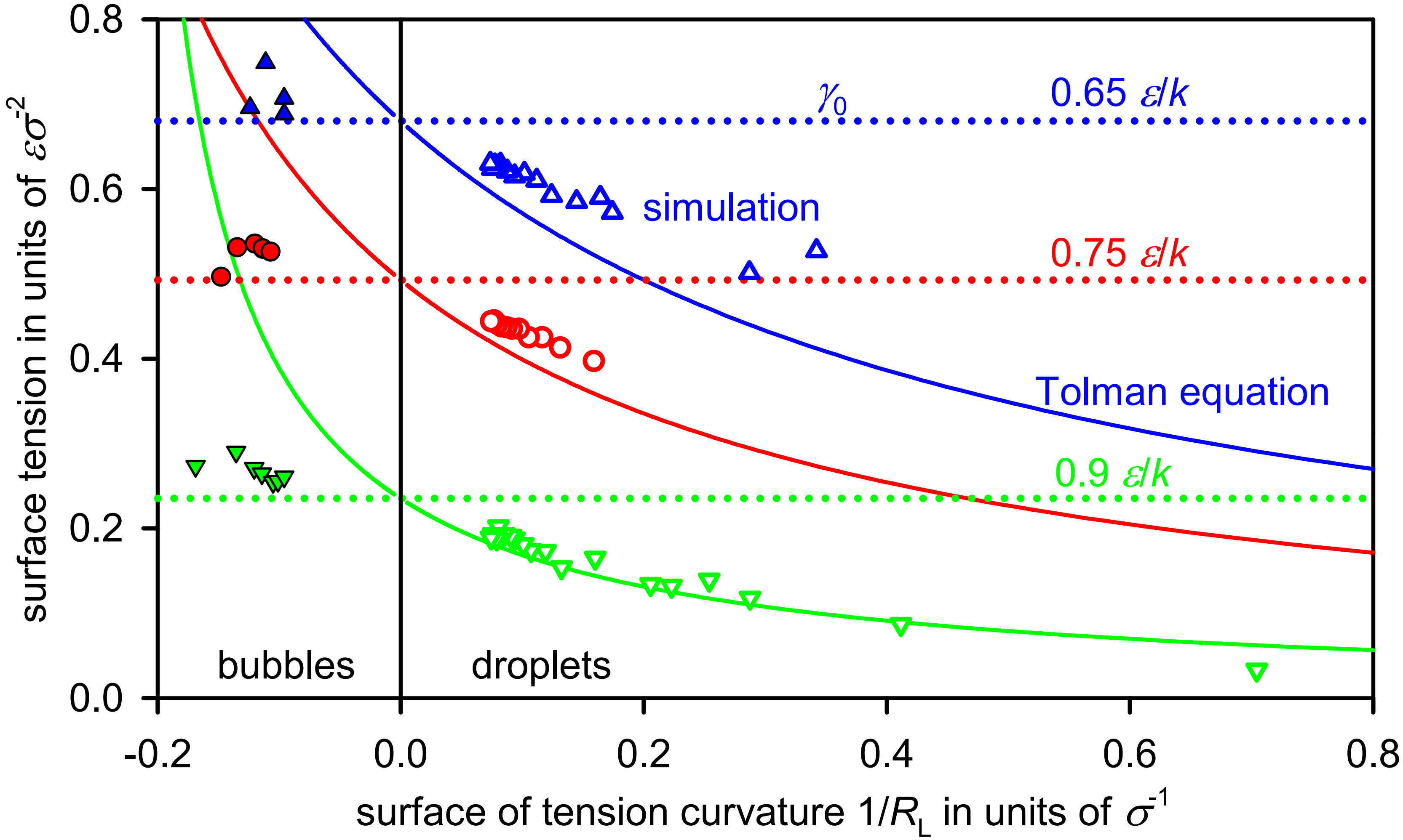
Bubble / negative curvature

Fluid density below saturation

Tolman length: simulation results



Surface tension: simulation results

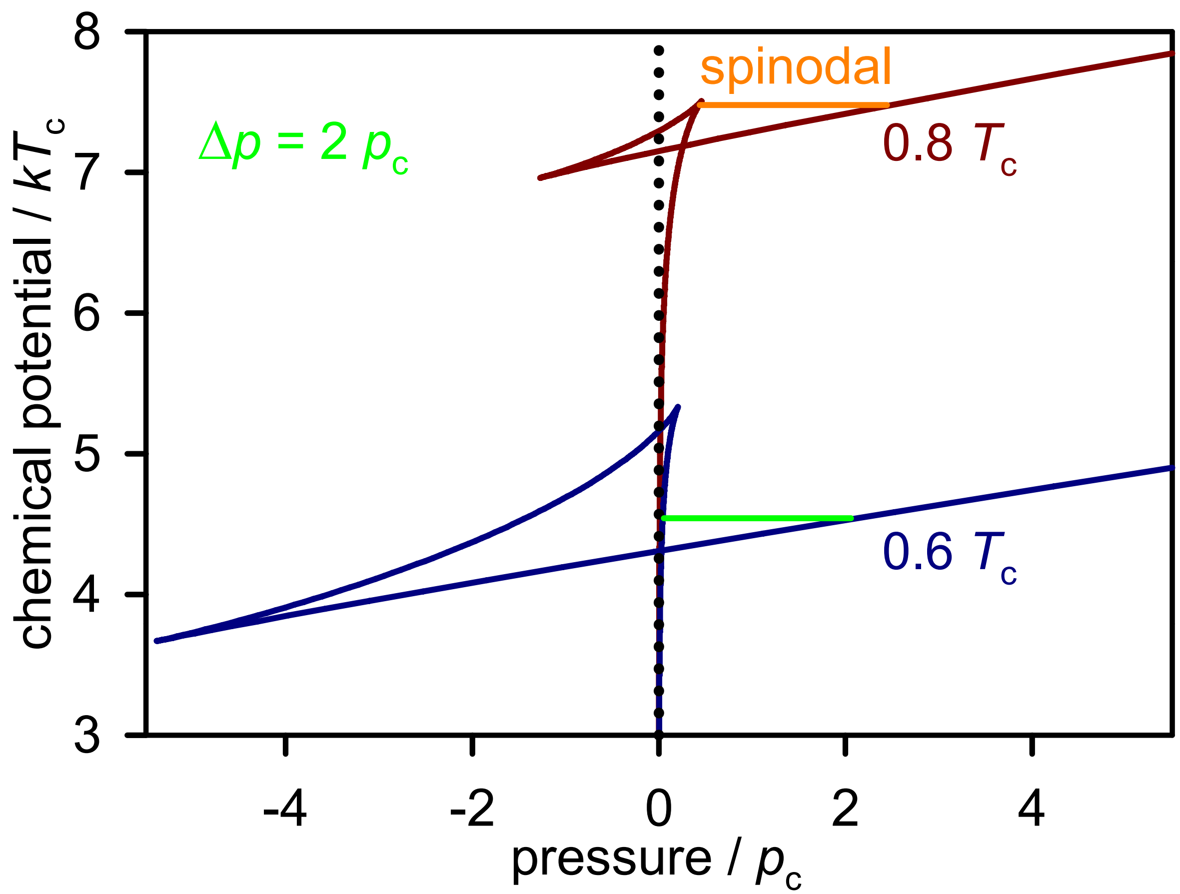


Tolman equation overestimates the influence of negative curvature on γ.

Phase equilibrium in the spinodal limit

$$\Delta p = \frac{2\gamma}{R_L}$$

Interpretation: On the spinodal, max(Δp) and min(R_L) coincide.



Droplet / positive curvature

Supersaturated fluid phases

min(R_L) on the spinodal line

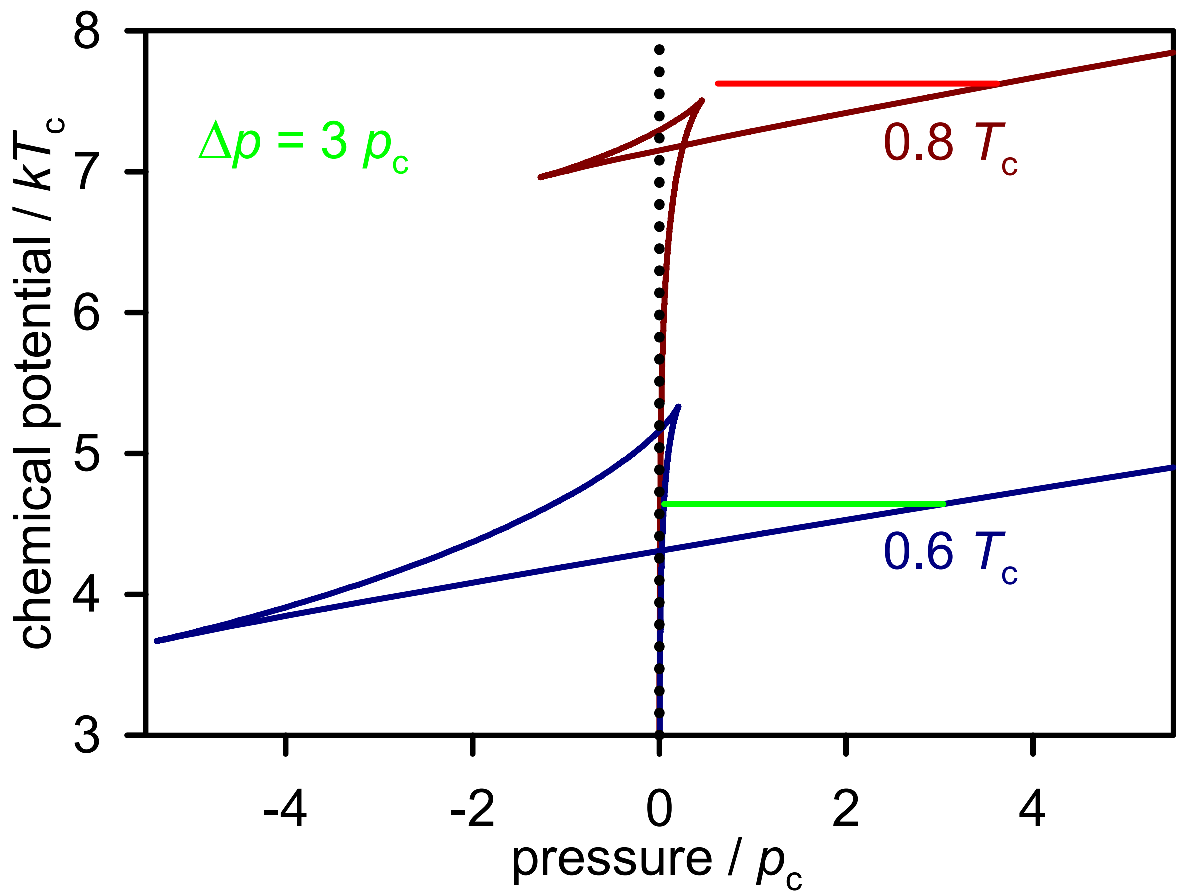
Bubble / negative curvature

Fluid density below saturation

No equilibrium beyond the spinodal limit

$$\Delta p = \frac{2\gamma}{R_\mathrm{L}}$$

The Laplace equation, γ, and R_L require an equilibrium.



Droplet / positive curvature

Supersaturated fluid phases

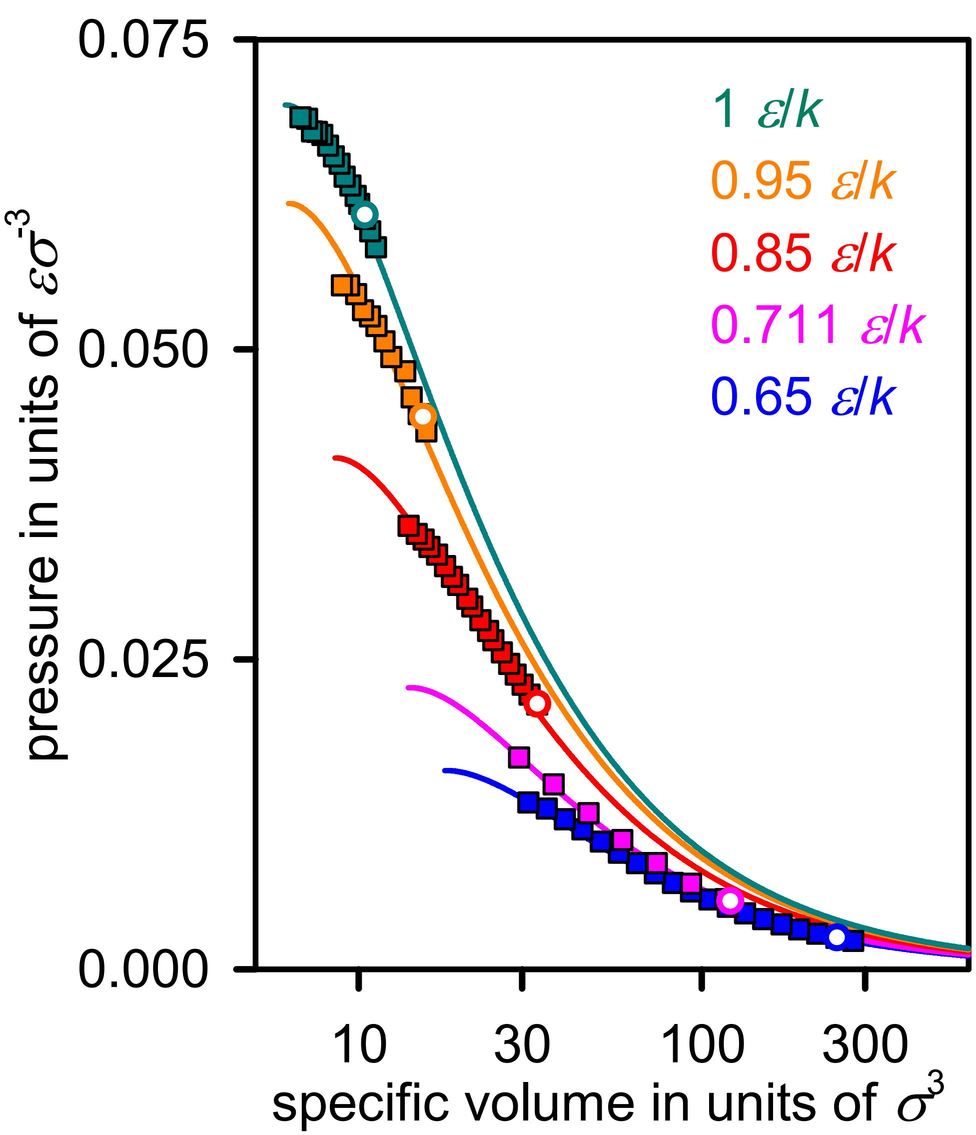
min(R_L) on the spinodal line

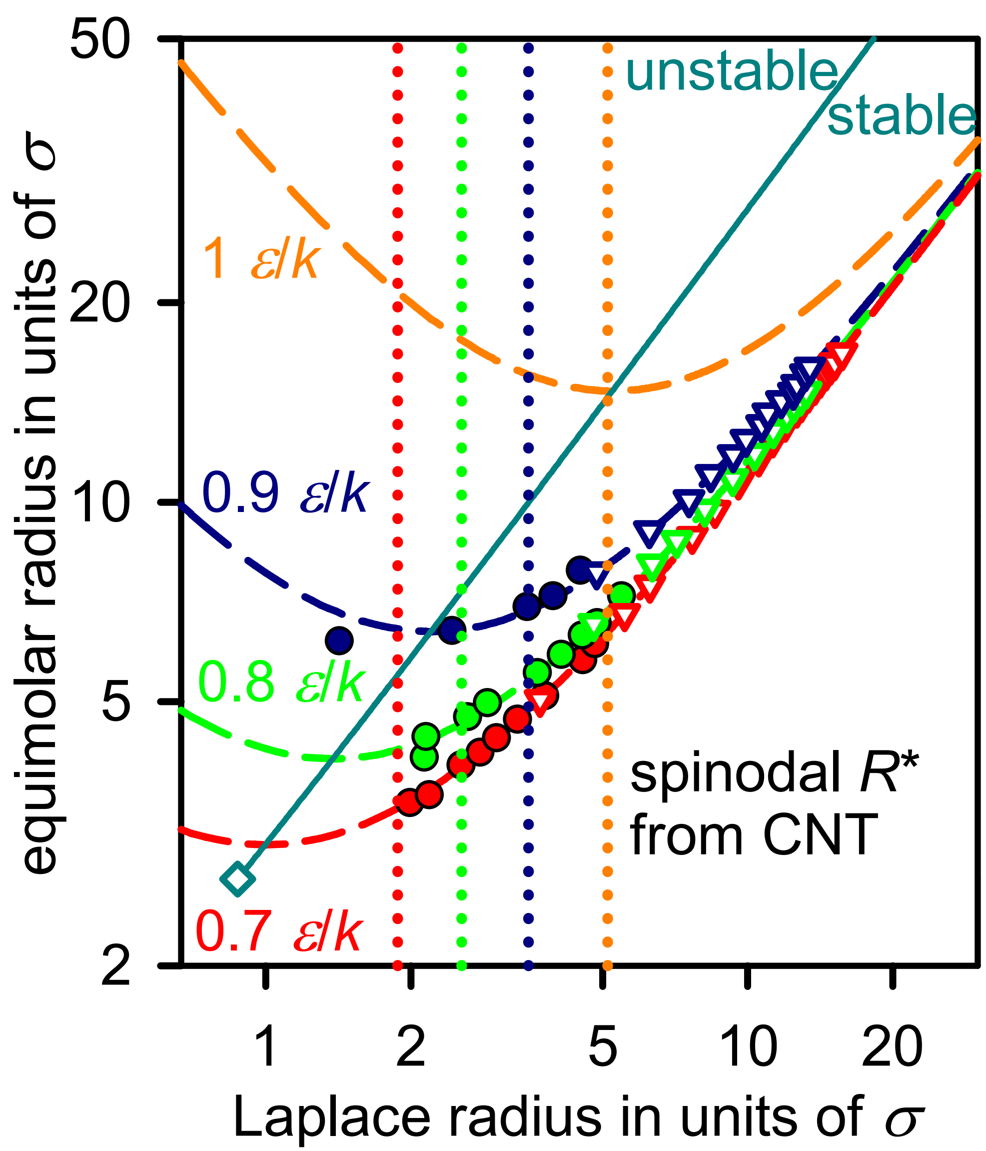
Smaller droplets cannot reach an equilibrium

Bubble / negative curvature

Fluid density below saturation

The stability limit for vapors and droplets





Innovative HPC-Methoden und Einsatz für hochskalierbare Molekulare Simulation (IMEMO)

Bundesministerium für Bildung und Forschung

October 2008 – December 2011

Project associates:

Industrial associates:

Conclusion

- MD simulation of **equilibria** allows sampling over an arbitrary time interval, eventually leading to the desired level of accuracy.
- Single **droplets** and **bubbles** are stable in the *NVT* ensemble.
- The maximal curvature that can be stabilized corresponds to **spinodal** conditions for the surrounding bulk phase.
- The **classical nucleation theory** leads to acceptable results for critical droplets in supersaturated vapors. However, it does not take into account curvature effects on the surface tension.
- The Tolman equation is accurate for droplets, but for bubbles it overestimates the curvature influence on the surface tension.