



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

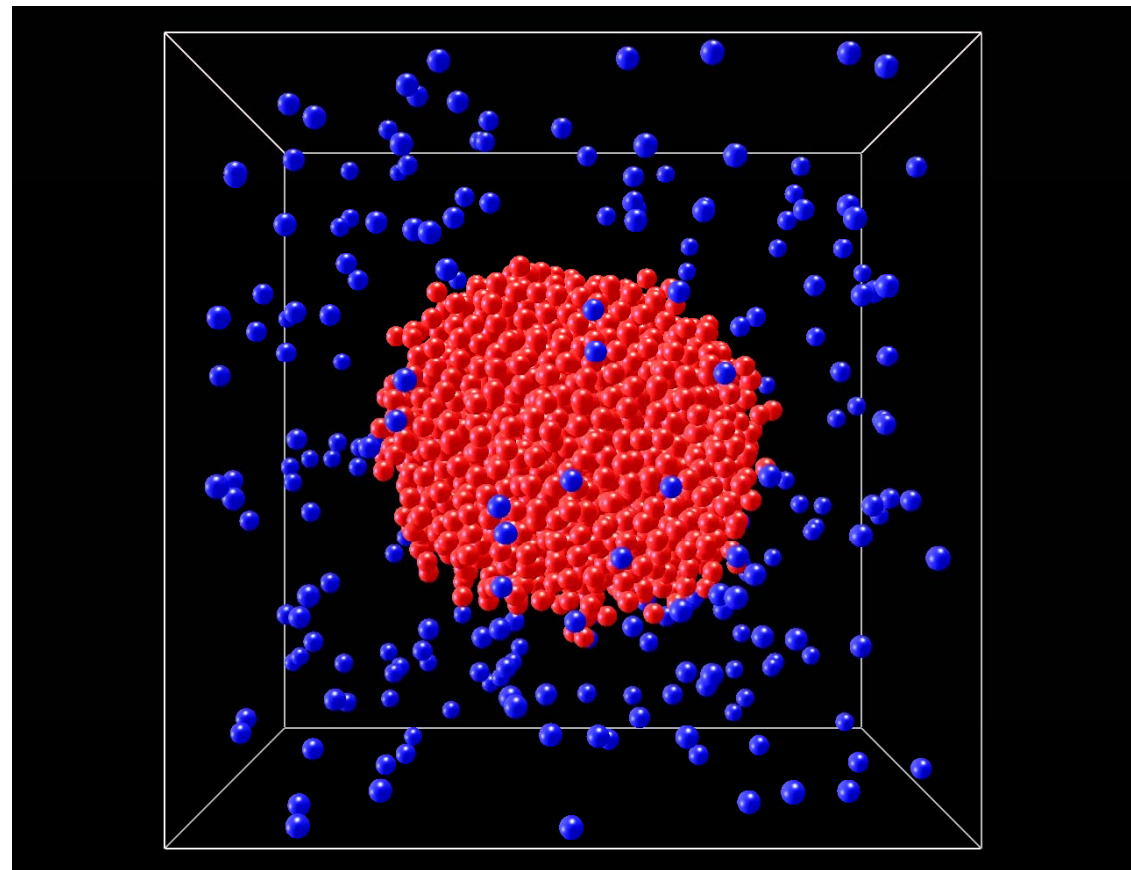
The curved vapor-liquid interface of the Lennard-Jones fluid

Taras Shevchenko Kyiv National University, May 23, 2010

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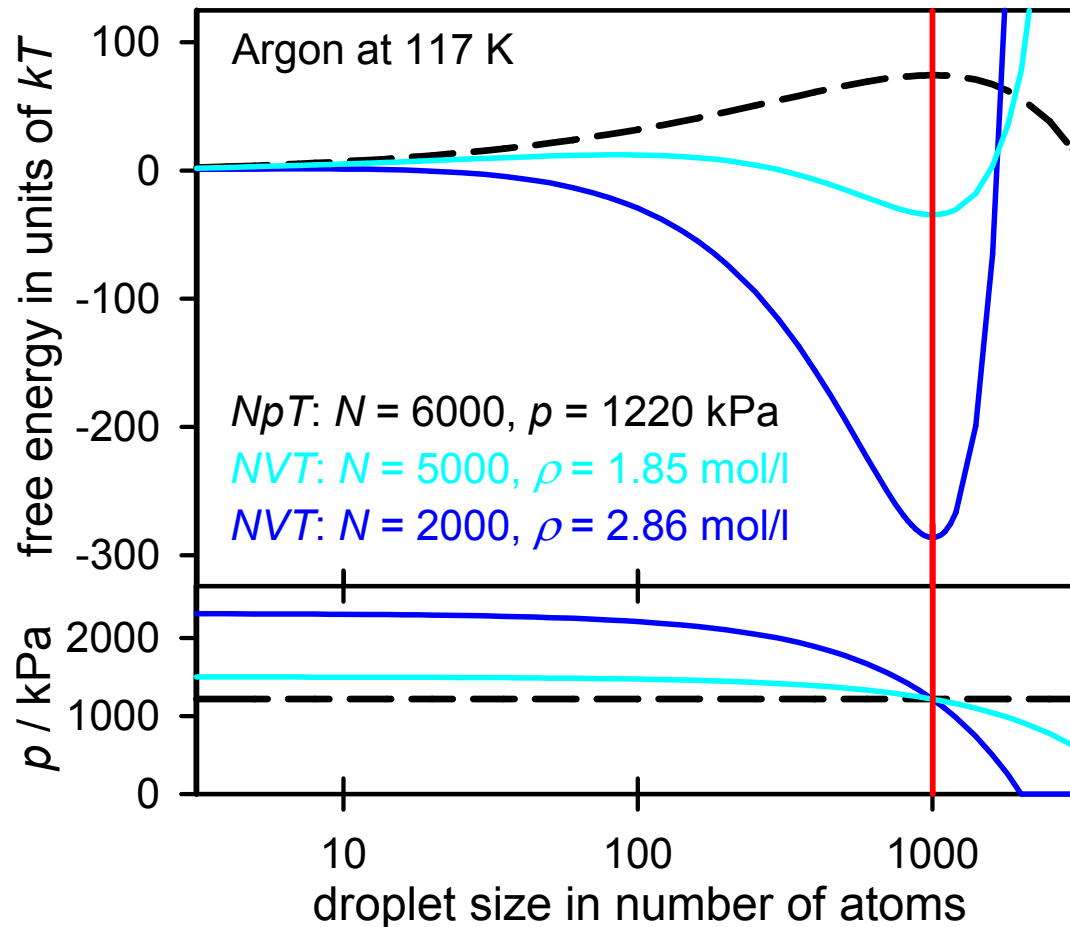
MD simulation of a single droplet

- 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 :

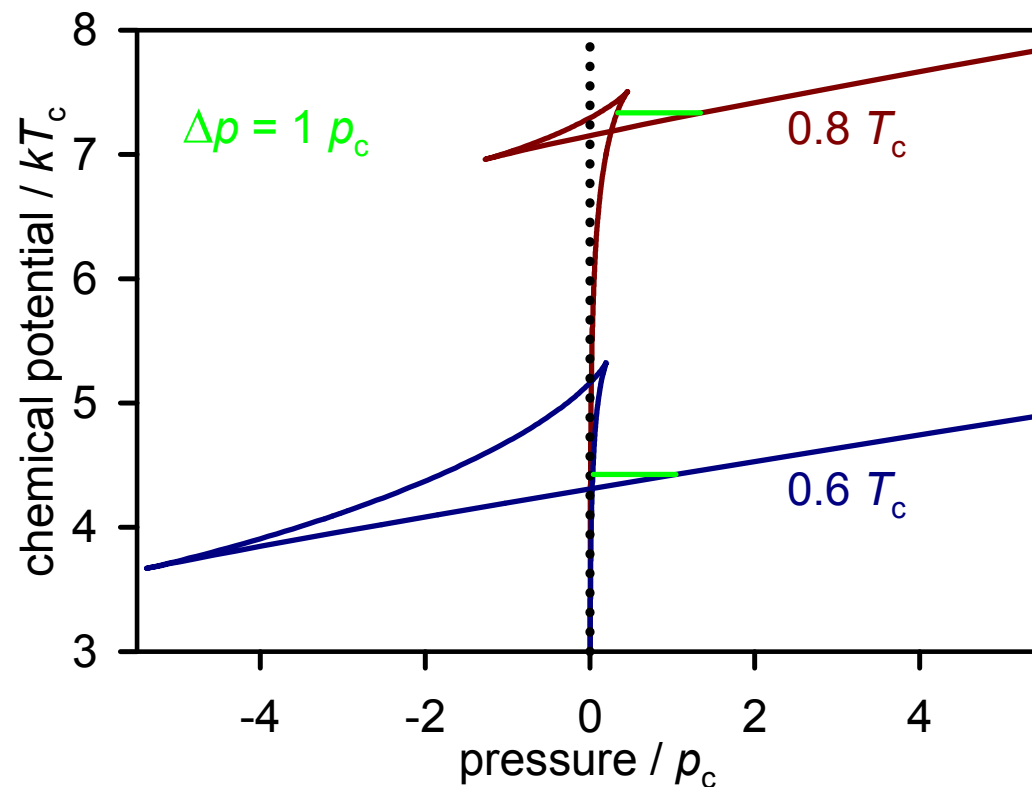
1 unstable equilibrium

1 stable equilibrium

Convex spherical interfaces in equilibrium

$$p_l - p_v = \frac{2\gamma}{R_L}$$

Interpretation: Definition of the Laplace radius R_L

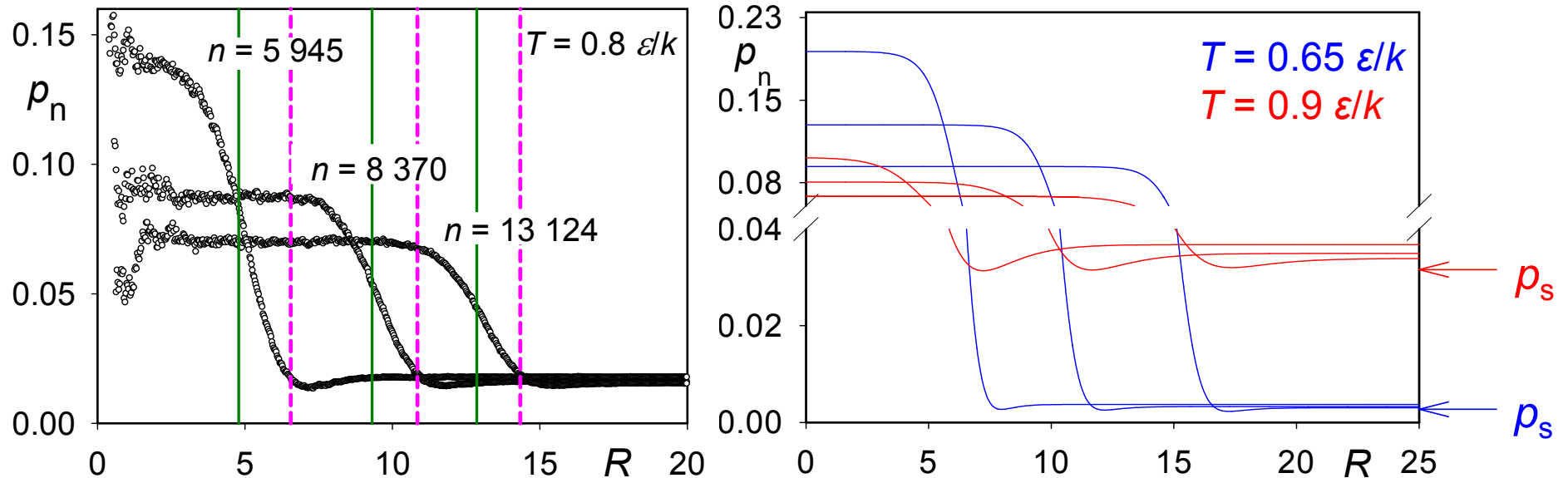


Droplet / positive curvature

Supersaturated fluid phases

Normal pressure profile

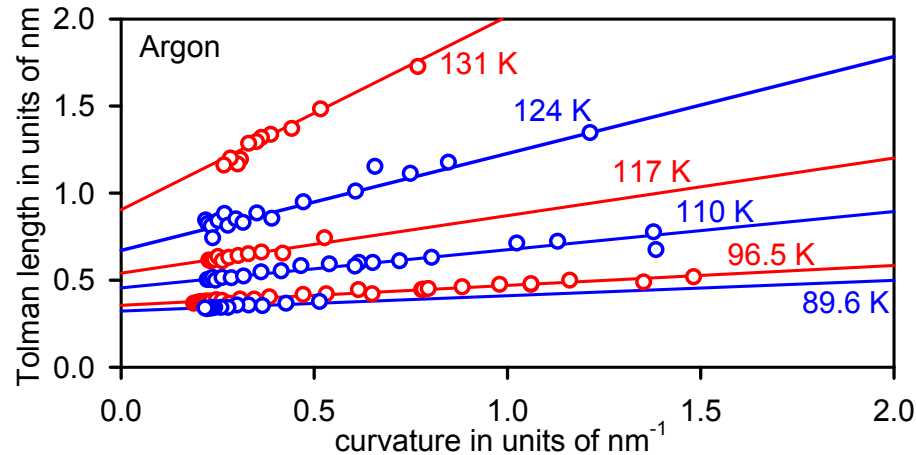
From the average Irving-Kirkwood pressure tensor in polar coordinates:



- - - Equimolar radius R_e
- Laplace radius R_L

$$\begin{aligned}
 p_v - 2p_n(R) + p_\ell &= (p_0 - p_v) \tanh(2D_v^{-1}[R - R_v]) \\
 &\quad + (p_\ell - p_0) \tanh(2D_\ell^{-1}[R - R_\ell])
 \end{aligned}$$

Droplet surface tension



For small droplets, the Tolman length

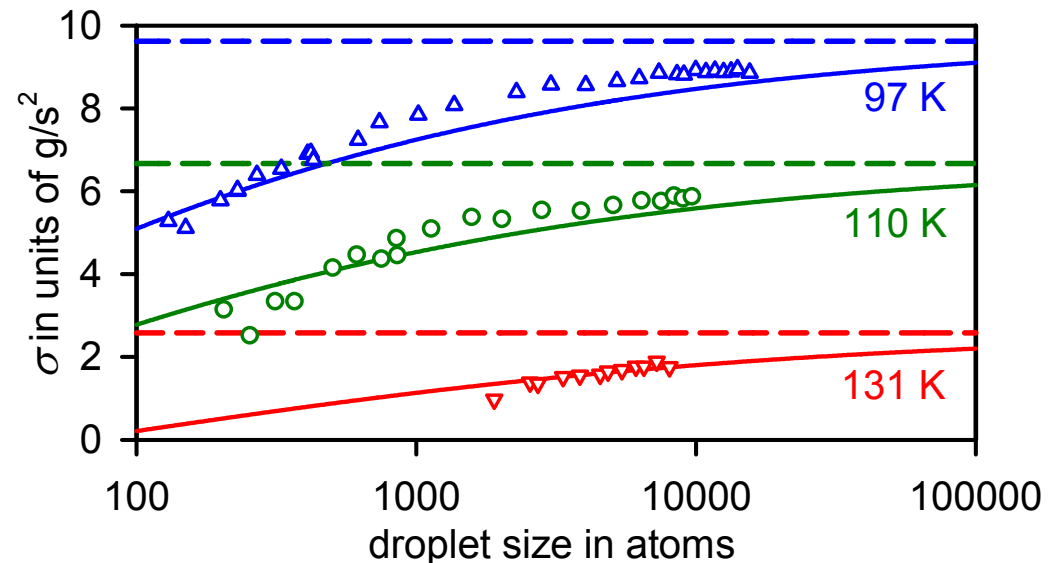
$$\delta = R_e - R_L$$

is significantly elevated.

Tolman equation:

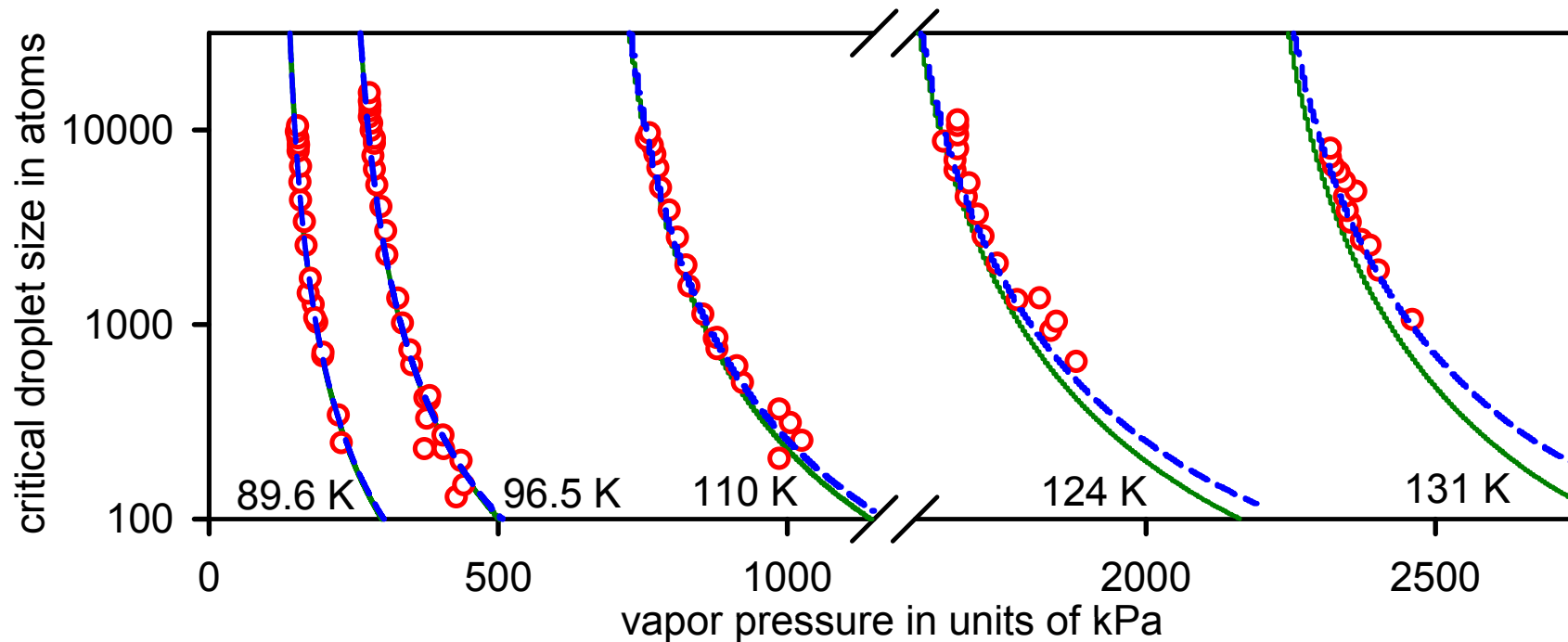
$$\frac{\gamma_\infty}{\gamma_0} \approx \frac{R_e + \delta_\infty}{R_e - \delta_\infty}$$

- simulation
- Tolman equation
- - - planar interface



Single droplet in equilibrium

Argon (truncated-shifted LJ model)



— “standard” CNT

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

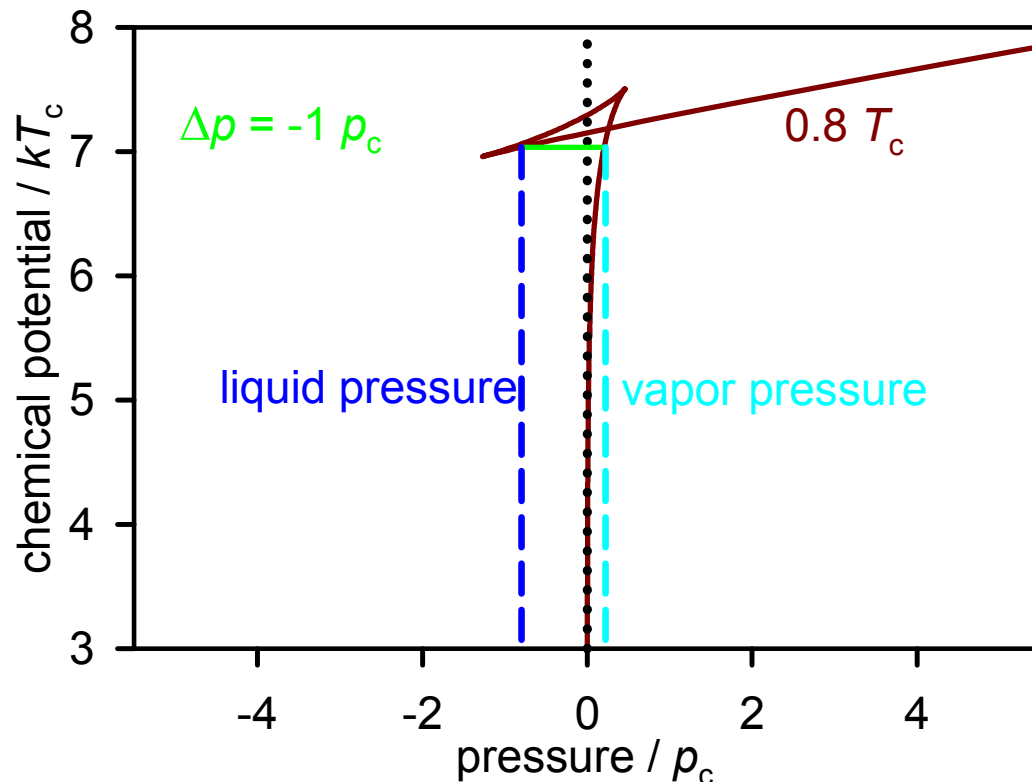
- - - CNT with the pressure effect

$$n^* = \left(\frac{2\gamma_0 a}{3\Delta\mu_{\text{eff}}} \right)^3$$

Concave spherical interfaces in equilibrium

$$p_l - p_v = \frac{2\gamma}{R_L}$$

Interpretation: The Laplace radius R_L is negative.



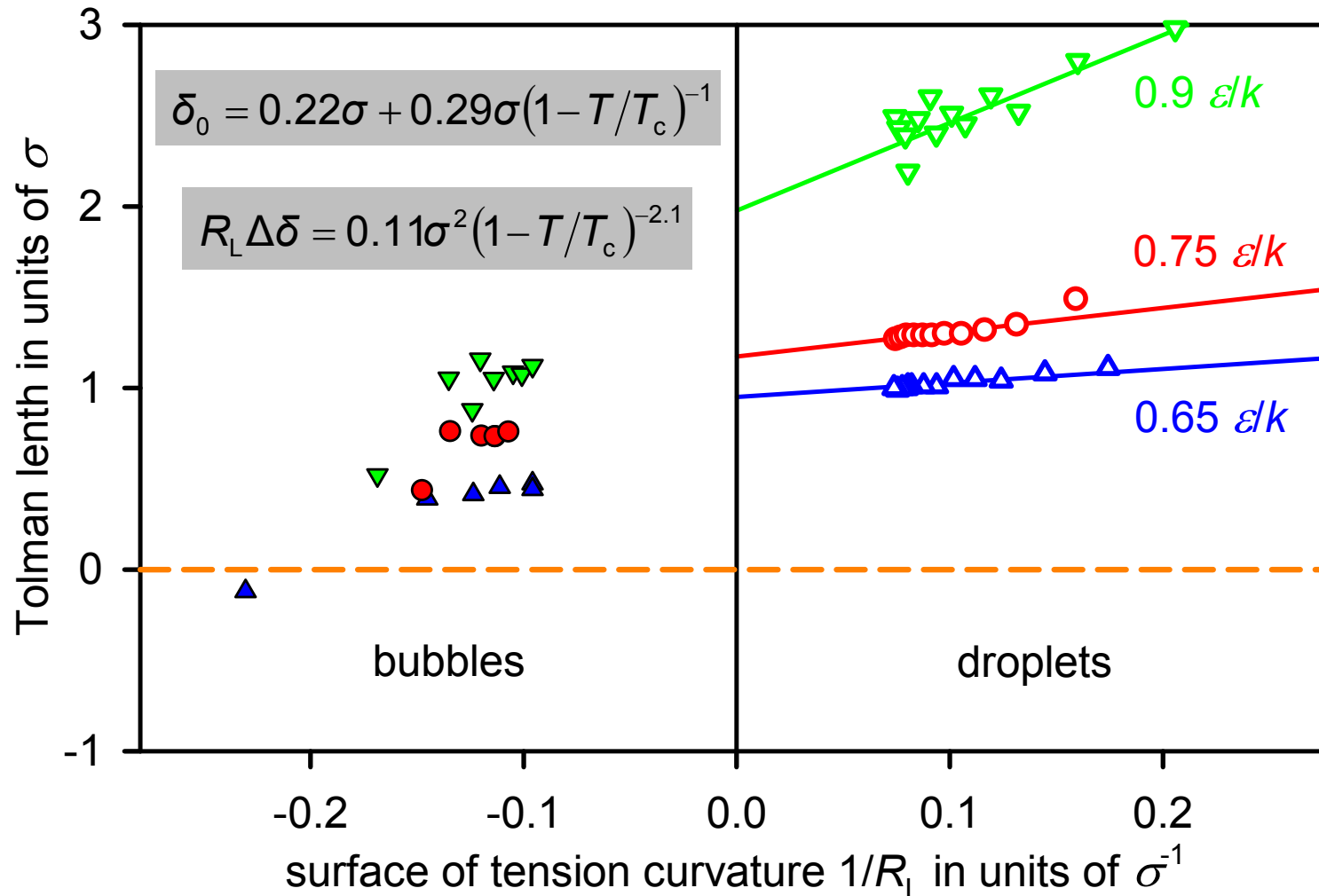
Droplet / positive curvature

Supersaturated fluid phases

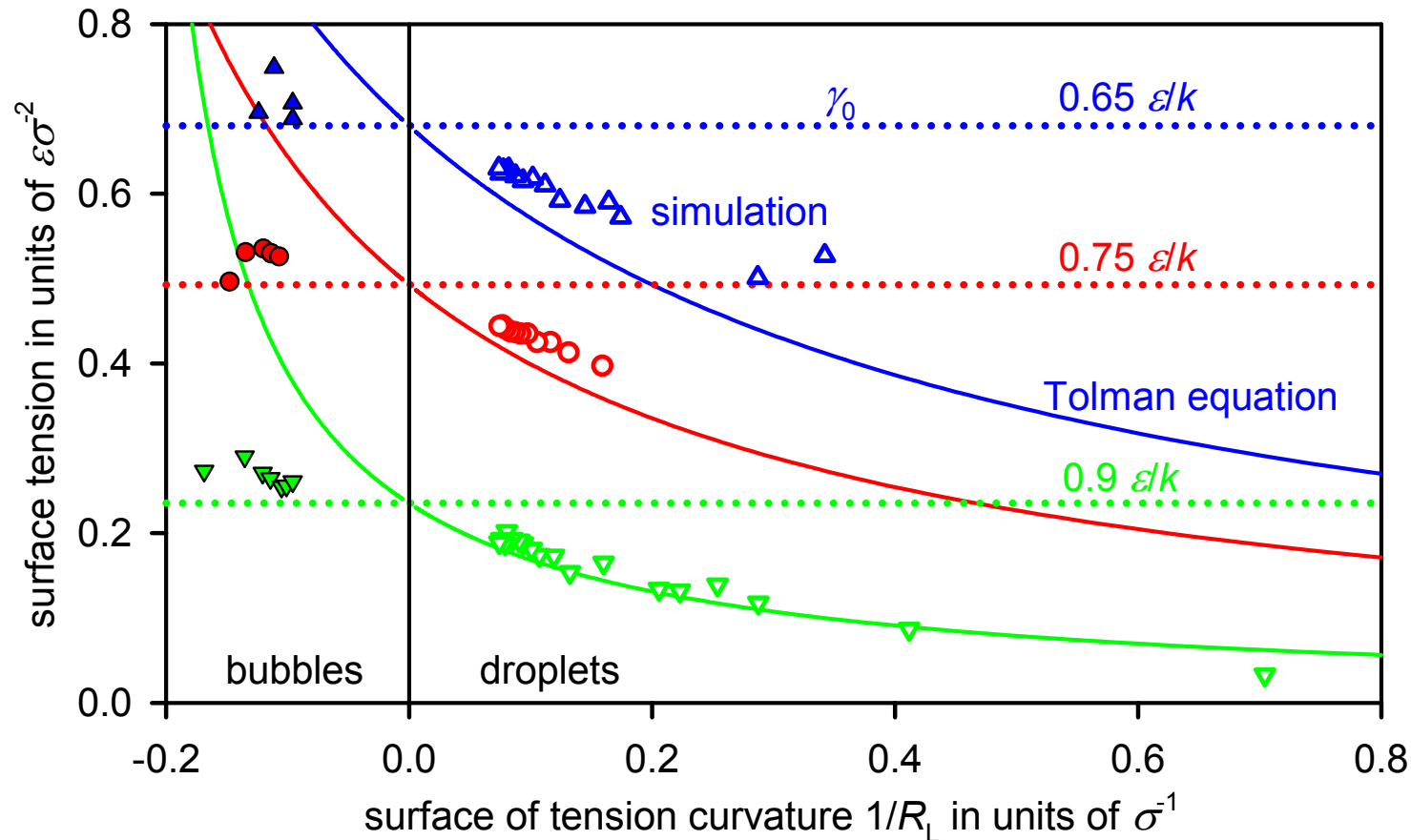
Bubble / negative curvature

Fluid density below saturation

Tolman length: simulation results



Surface tension: simulation results

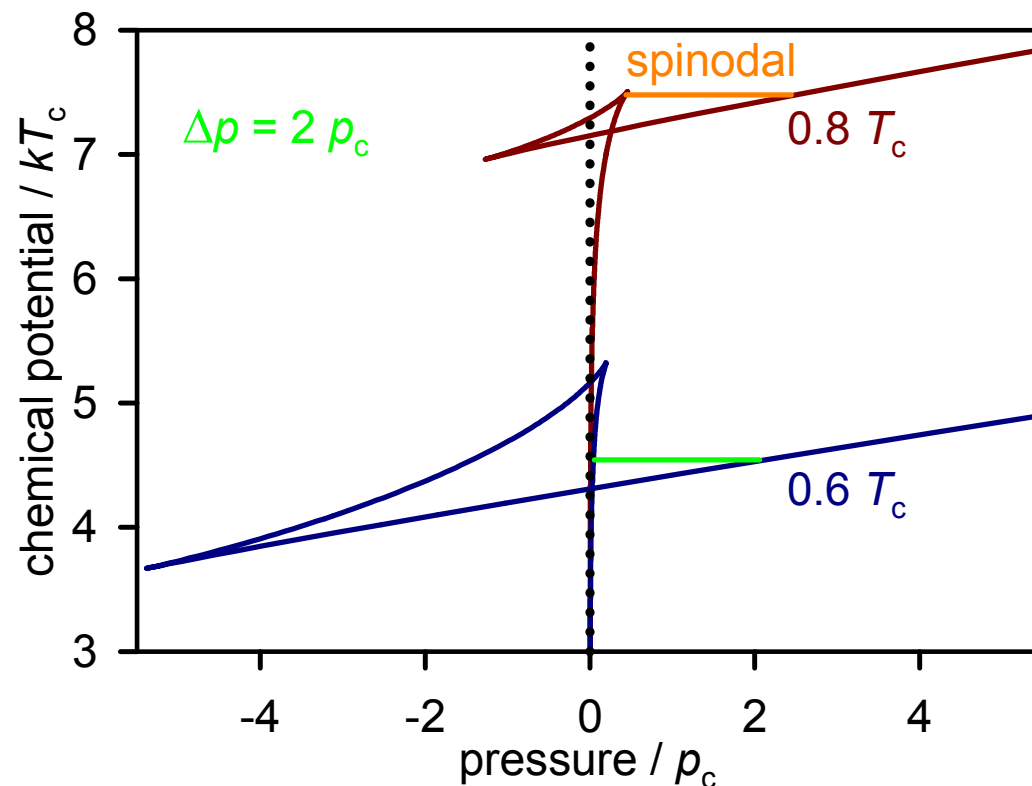


Tolman equation overestimates the influence of negative curvature on γ .

Phase equilibrium in the spinodal limit

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

Interpretation: On the spinodal, $\max(\Delta p)$ and $\min(R_L)$ coincide.



Droplet / positive curvature

Supersaturated fluid phases

$\min(R_L)$ on the spinodal line

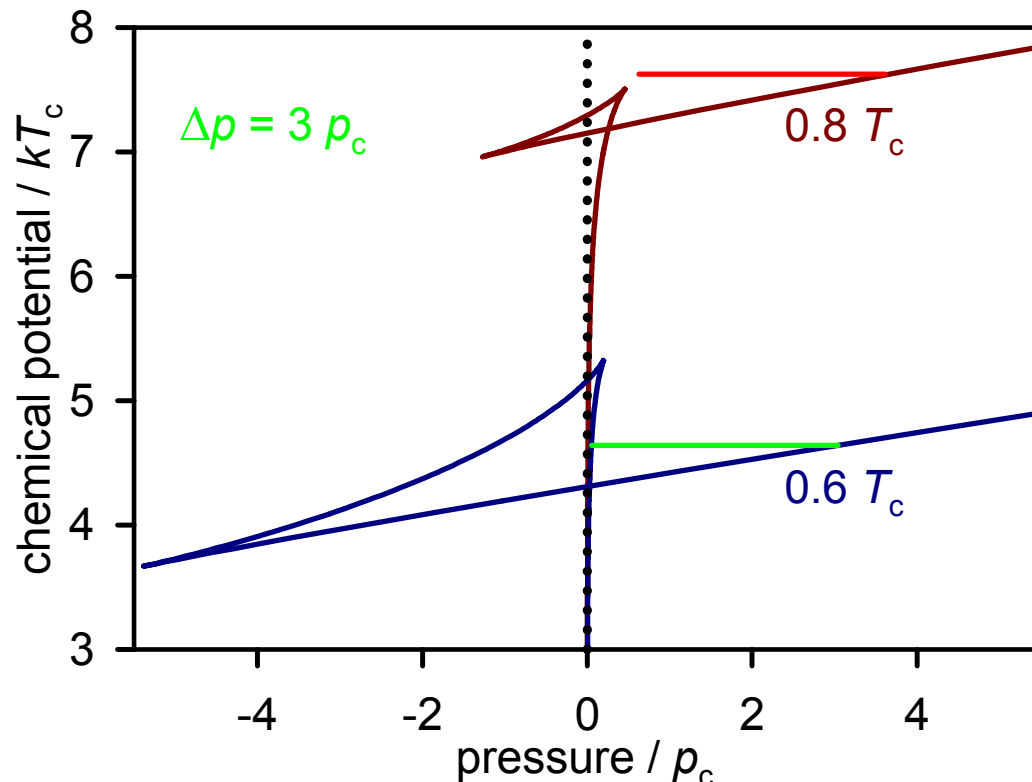
Bubble / negative curvature

Fluid density below saturation

No equilibrium beyond the spinodal limit

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

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



Droplet / positive curvature

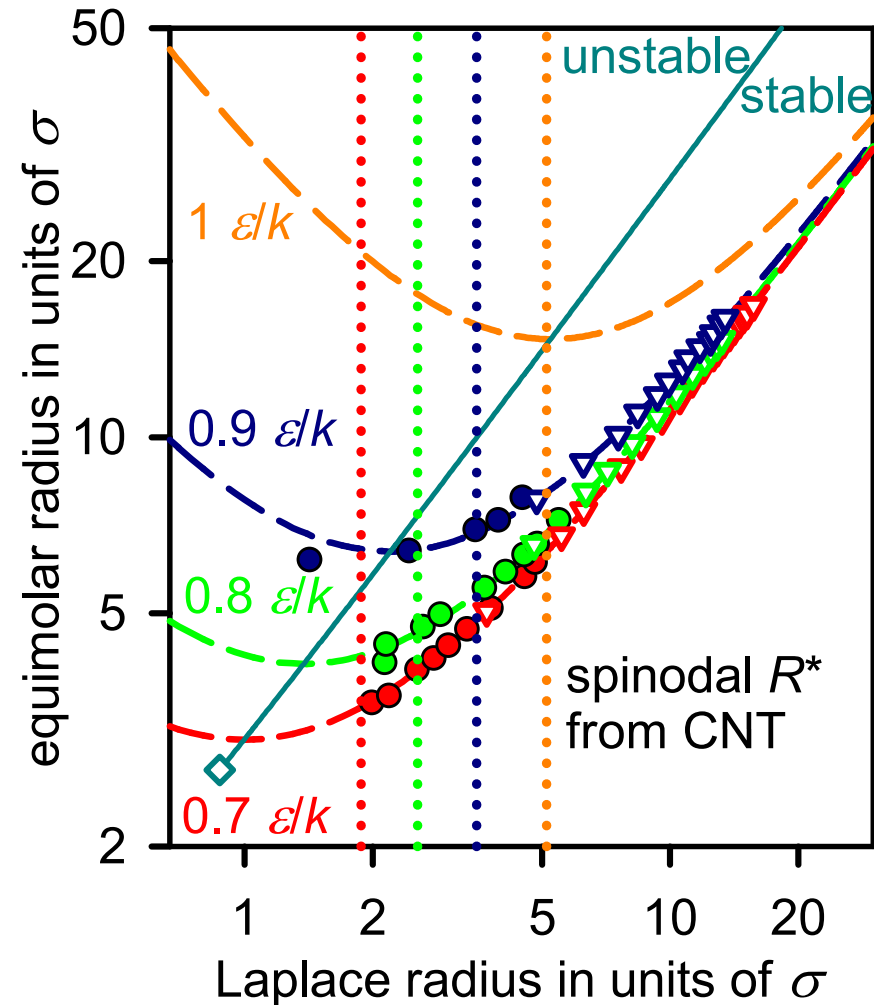
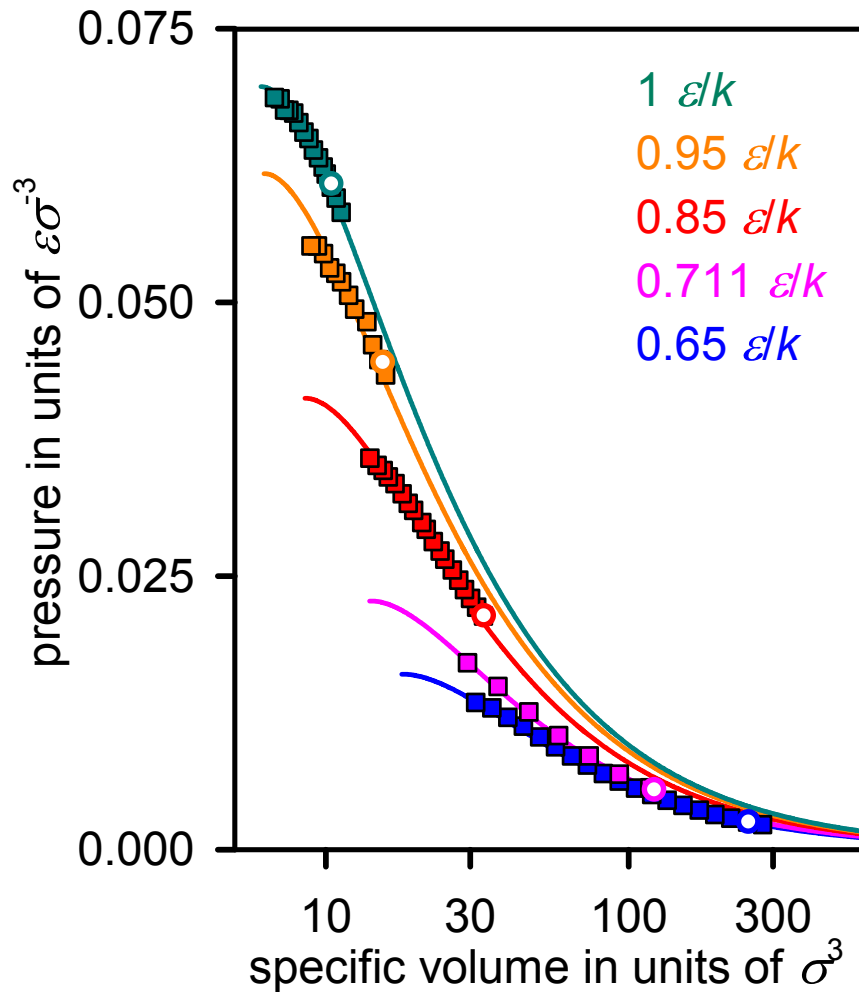
Supersaturated fluid phases
 $\min(R_L)$ on the spinodal line

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:

H L R I S



 TECHNISCHE UNIVERSITÄT
KAISERSLAUTERN

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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.