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Surface property corrections to the classical nucleation theory

Kensington, 18th October 2010

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Bundesministerium für Bildung und Forschung

DAAD Deutscher Akademischer Austausch Dienst German Academic Exchange Service

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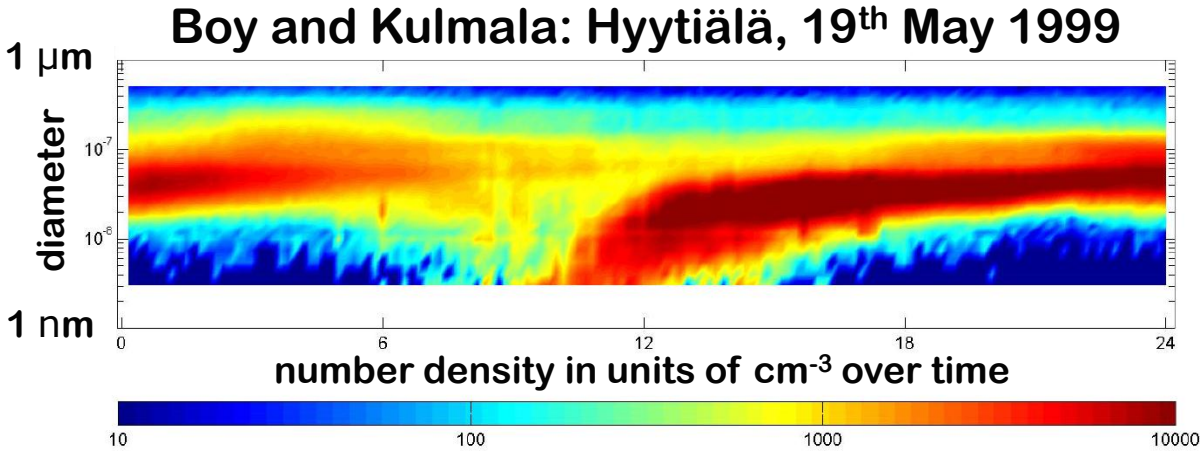
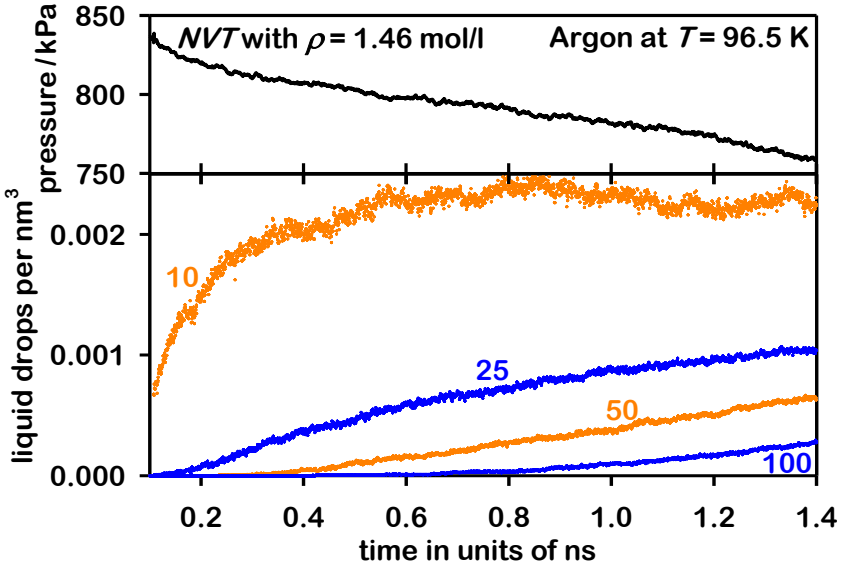
MD simulation of nucleation (I)



Yasuoka and Matsumoto (1998):

- Canonical MD simulation
- Limited time interval
- Conditions change over time



MD simulation of nucleation (II)

- Integration time step: typically between 2 and 5 fs

- Feasible simulation time: on the order of nanoseconds

- A saturated vapour with a volume of 10^{-20} m^3 contains:
  800 000 molecules (saturated methane at 114 K)
  7 000 000 molecules (saturated CO_2 at 253 K)

- Minimal nucleation rate accessible by direct simulation:

#nuclei / (volume V x time Δt) = nucleation rate J

10 / (10^{-20} m^3 x 10^{-9} s) = 10^{30} / m^3s

experiment		direct MD simulation
up to 10^{23} / m^3s	⟷	above 10^{30} / m^3s

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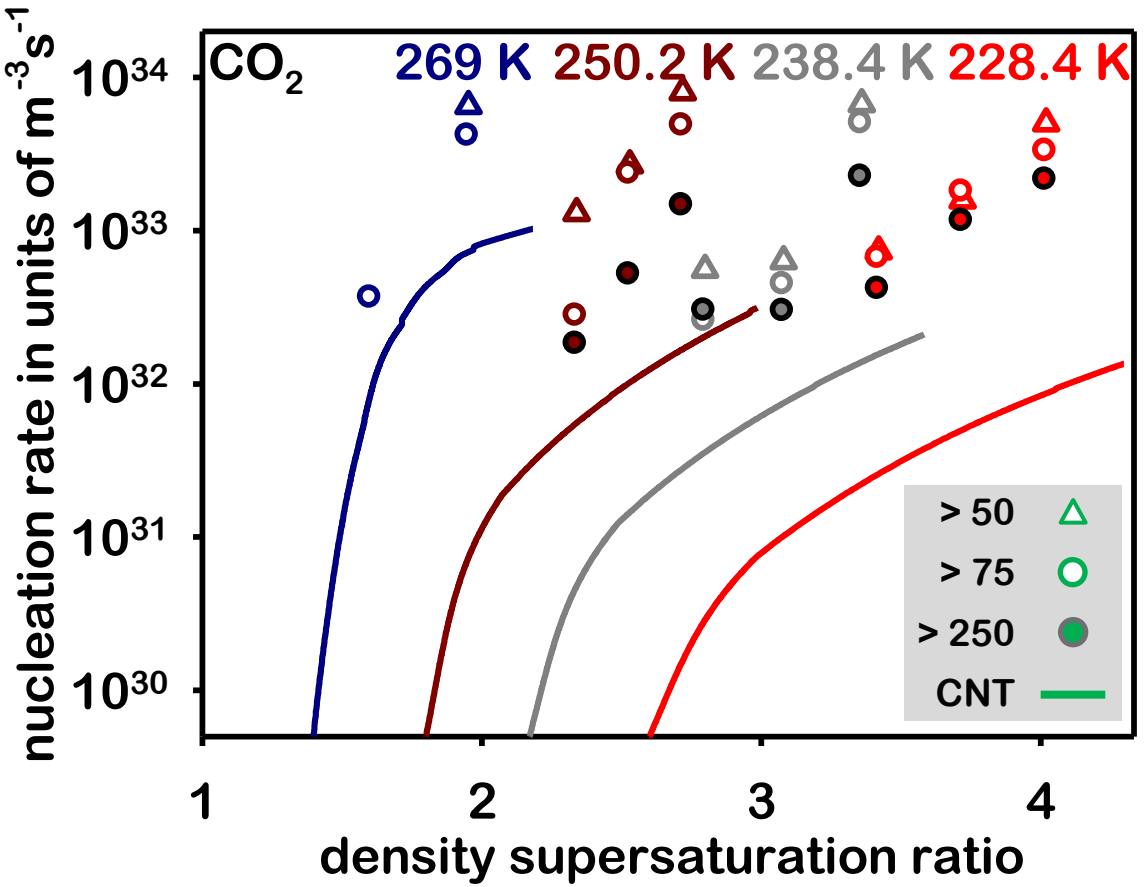
MD simulation of nucleation (III)

CH_4, C_2H_6, CO_2: Good agreement with classical nucleation theory.

CNT:

- Capillarity
  $\gamma = \gamma_0$,
- incompressible,
- spherical drops,
- collision rate
  $\rho(2\pi m T)^{-1/2}$.



MD simulation of nucleation (IV)

Typical scenario:

- *k* component vapour
- nearly pure liquid

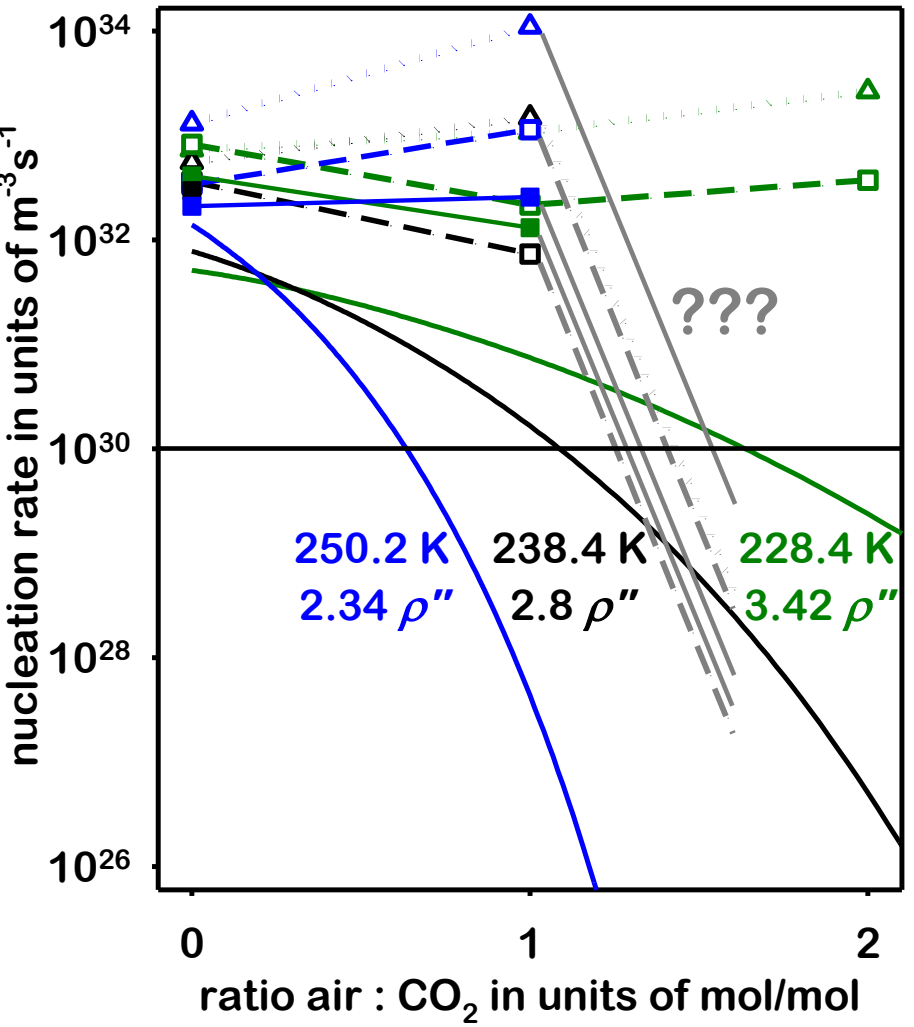
The other $k-1$ components have a "carrier gas" effect:

- thermalization
- "work" of the drop

Opposite influences on *J* …

— CNT / Wedekind *et al.*

△ > 50 ▫ > 100 ■ > 150



McDonald's dæmon (I)

Grand canonical MD simulation (Cielinski):

- test insertion/deletion steps alternating with MD steps
- fixed values of μ, V, and T
- test insertion of a molecule at a random position:

$$P = \min\left(1, \exp\left(\frac{\mu - \Delta U_{\text{pot}}}{T}\right)\frac{V}{\Lambda^3 (N+1)}\right)$$

- test deletion of a random molecule

$$P = \min\left(1, \exp\left(\frac{-\mu - \Delta U_{\text{pot}}}{T}\right)\frac{V}{\Lambda^3 N}\right)$$

- equal number of insertions and deletions ($\approx 10^{-4}\ N$ per step)

→ Stationary sampling of the supersaturated state …

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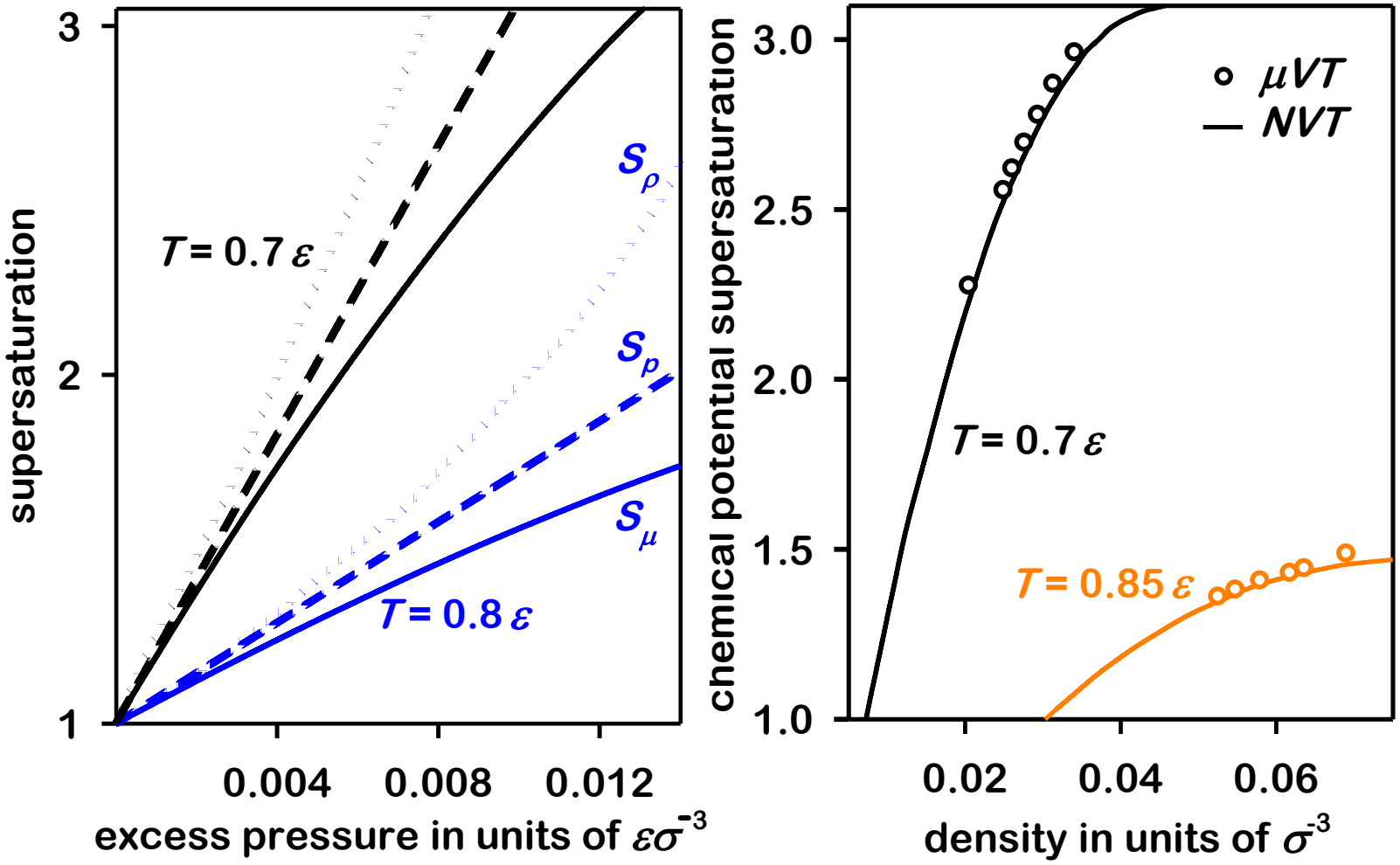
McDonald's dæmon (II)



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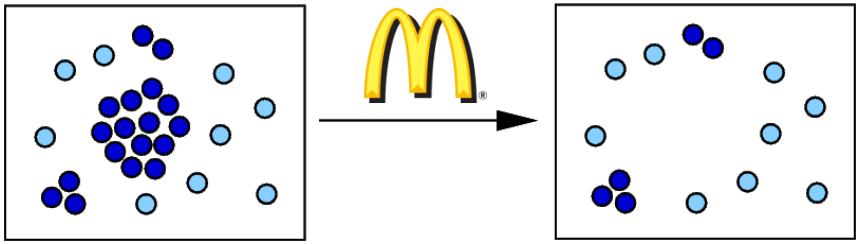
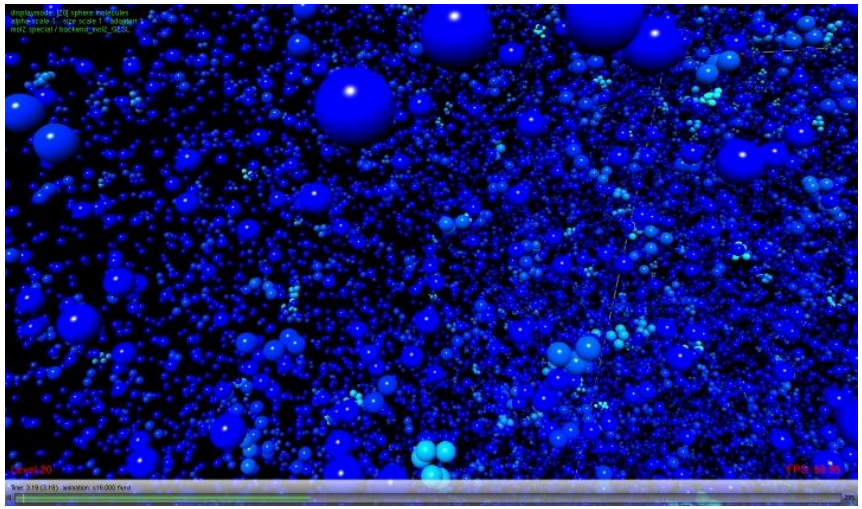
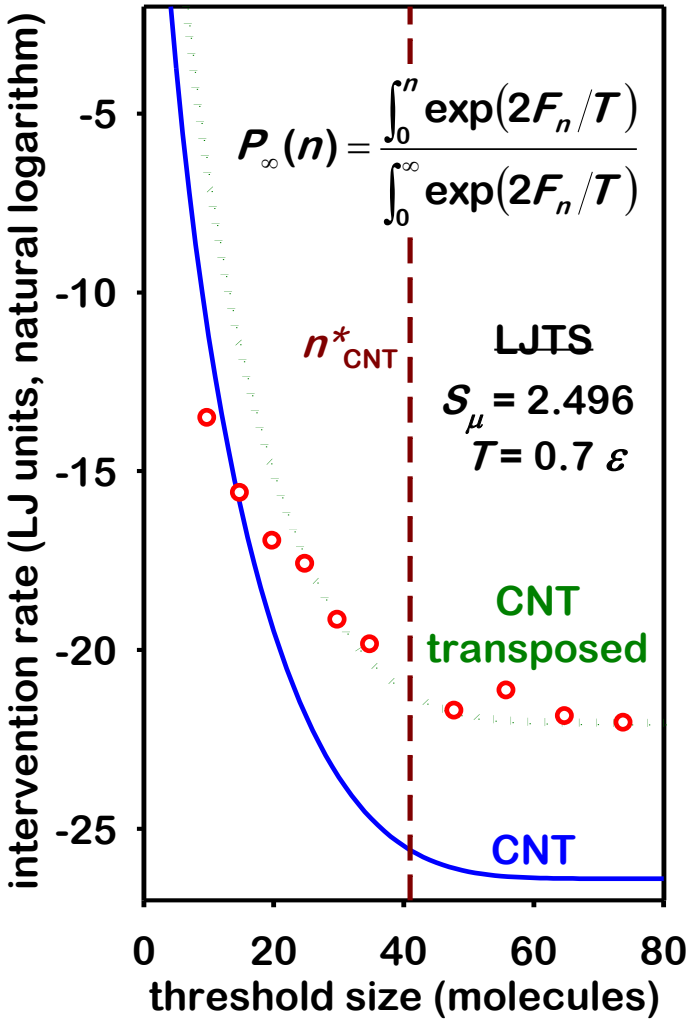
McDonald's dæmon (III)

Requirement for a steady state:

Elimination of liquid drops …







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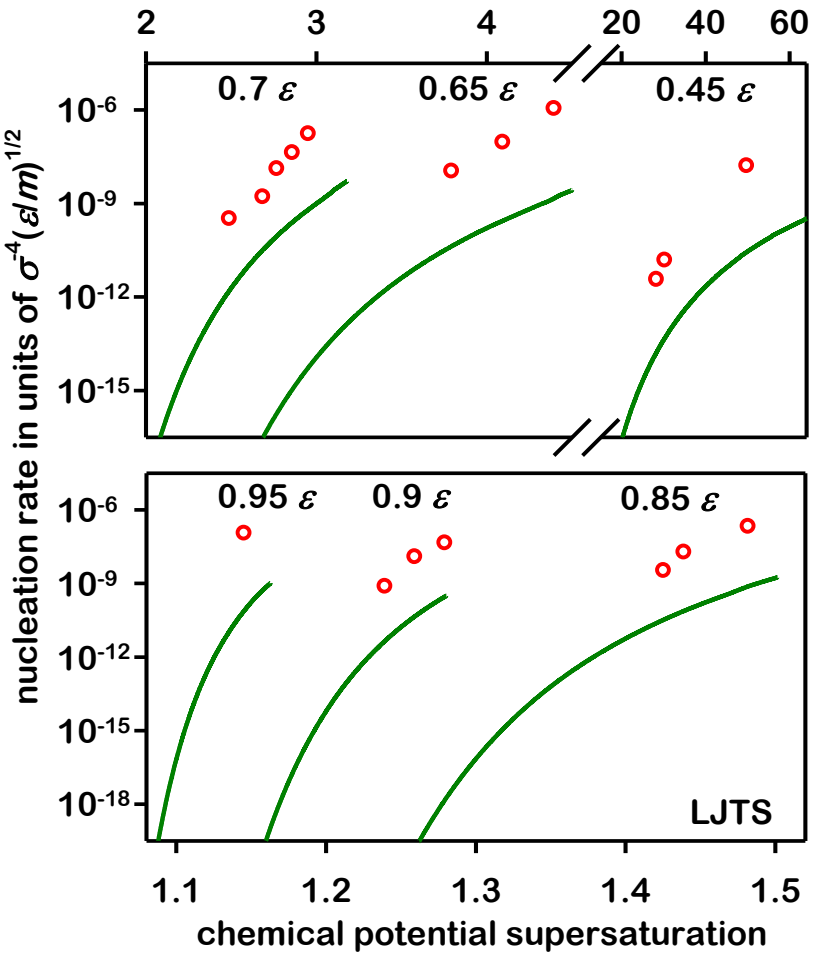
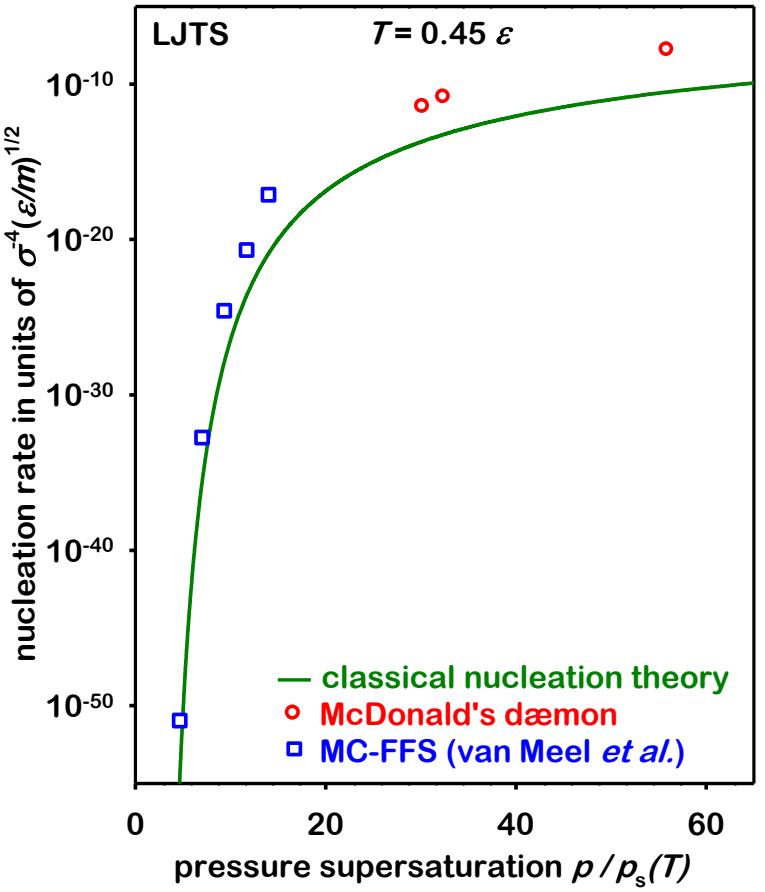
McDonald's dæmon (IV)





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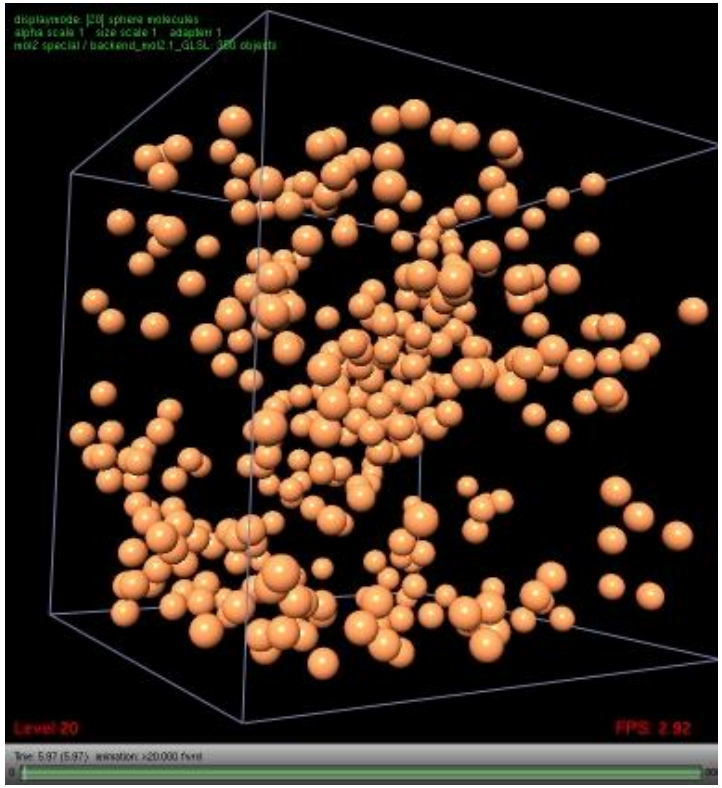
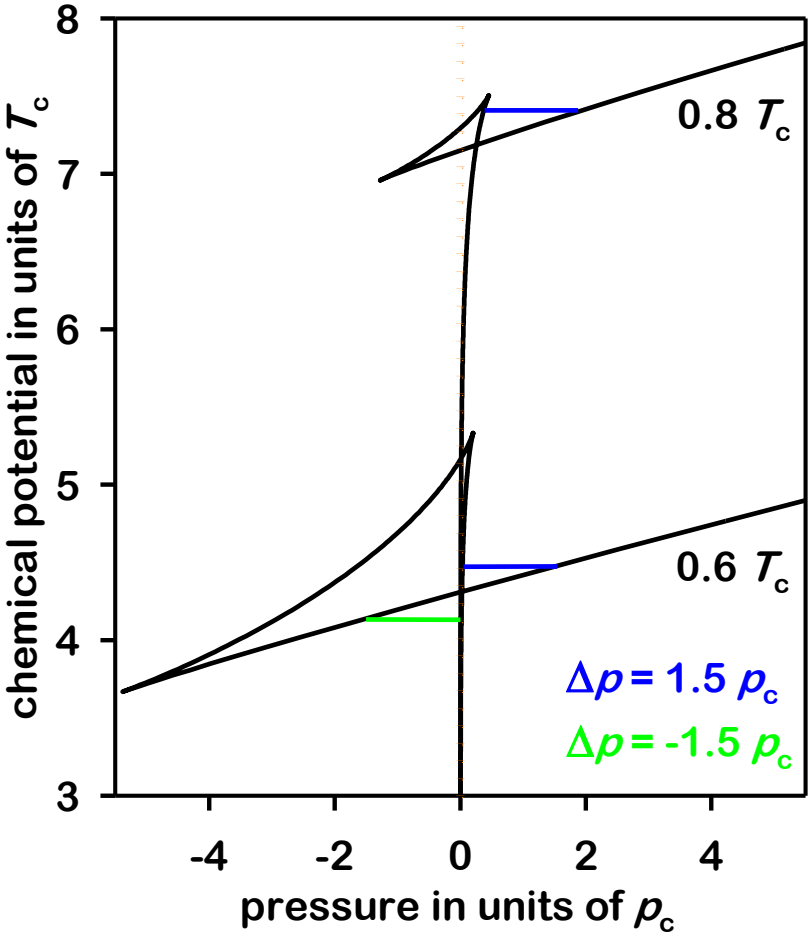
The critical liquid drop size (I)

Curved vapour-liquid equilibria:

- Liquid drop, metastable vapour
- Gas bubble, metastable liquid



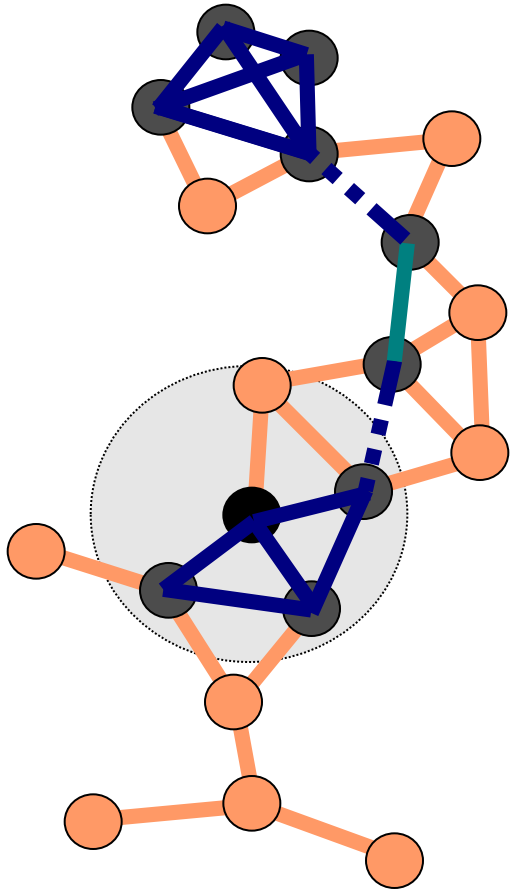


The critical liquid drop size (II)

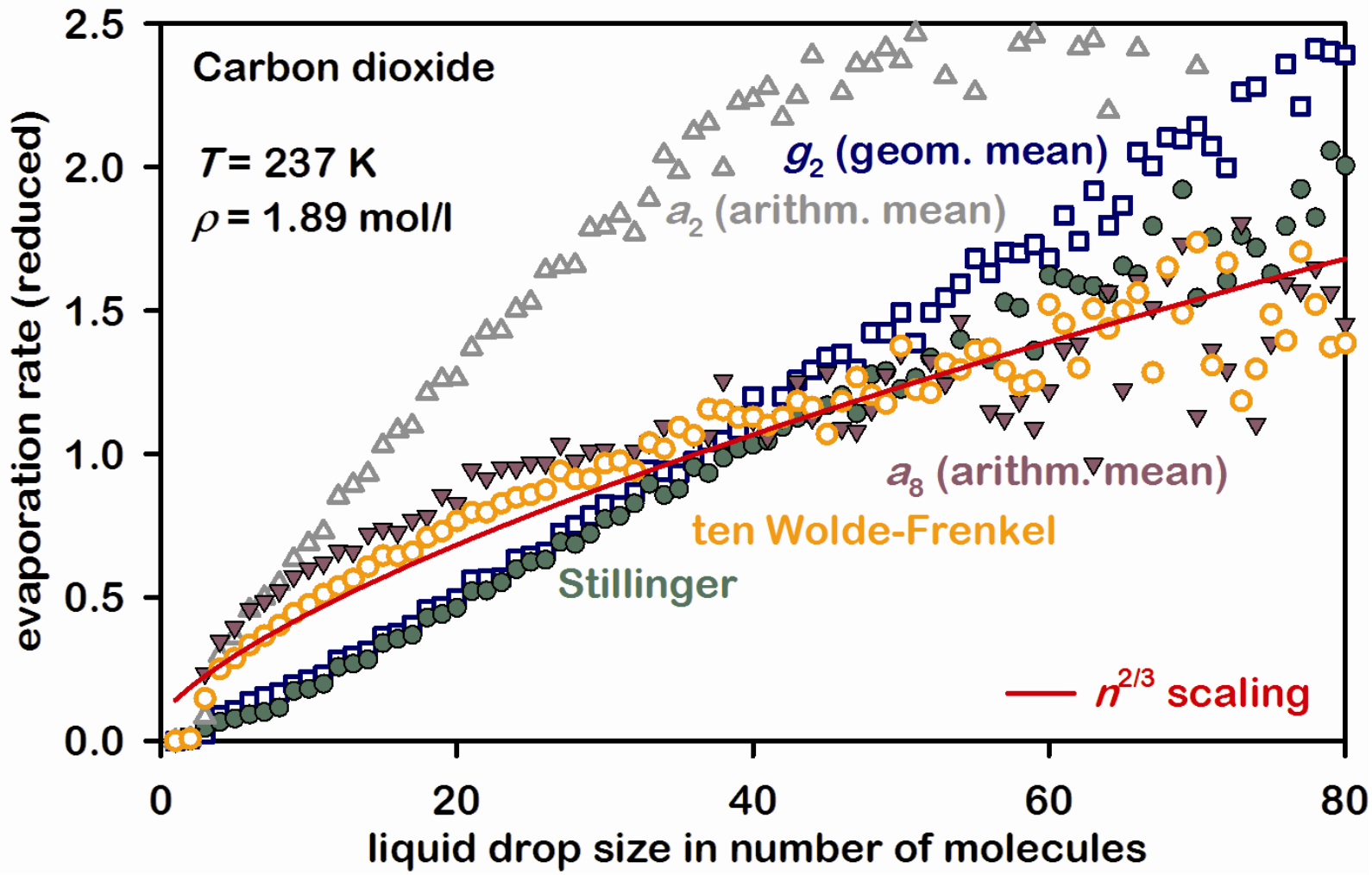
Cluster criteria for the liquid phase:

Stillinger: molecules with a distance of 1.5σ or less are liquid.
Ten Wolde and Frenkel (TWF): molecules with at least four neighbors within a distance of 1.5σ are liquid.
Arithmetic mean, *n* neighbors (a_n): a molecule is liquid if the density in the sphere containing its *n* nearest neighbors exceeds $(\rho'+\rho'')/2$.
Geometric mean, *n* neighbors (g_n): analogous, the required density is $(\rho'\rho'')^{1/2}$.

Nuclei can also be determined as **biconnected** (instead of connected) components, such that no nucleus can be separated by removing a single molecule (TWF' and g'_2 criteria).



The critical liquid drop size (III)



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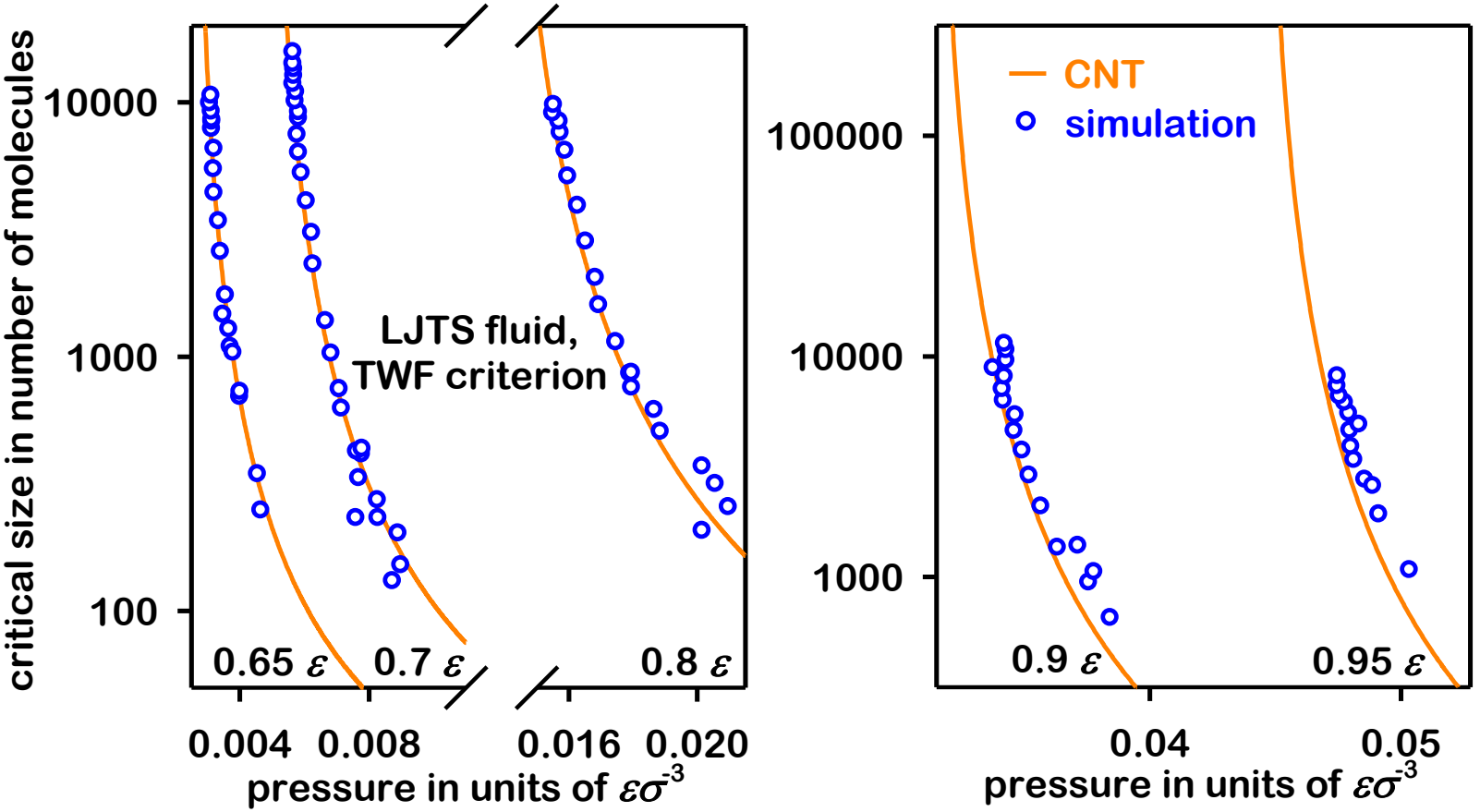
The critical liquid drop size (IV)



Simulation results confirm the classical predictions for n^*.

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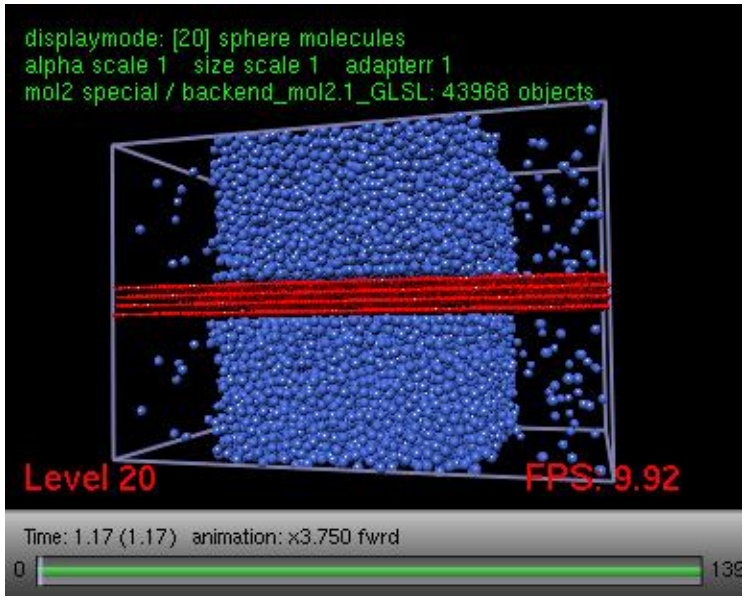
Tolman theory and cylindrical interfaces (I)

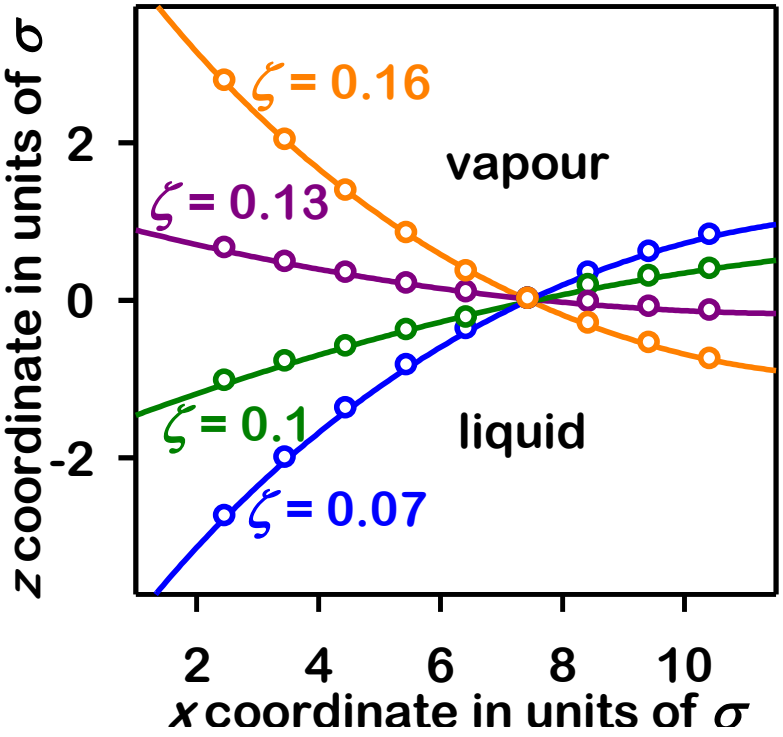
Simulation approach

LJTS fluid, generic wall model,
Dispersive energy $\varepsilon_{fw} = \zeta\varepsilon$



Equilibrium state

Cylindrical meniscus,
based on arithm. mean density



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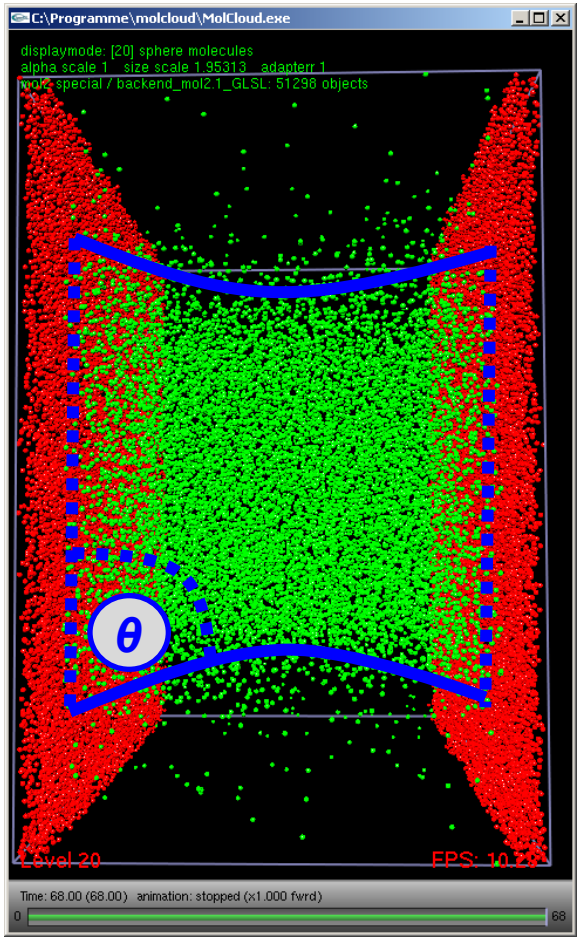
Tolman theory and cylindrical interfaces (II)



Gibbs adsorption eqn.

$$d\gamma = -\Gamma d\mu$$

Tolman (cylindrical)

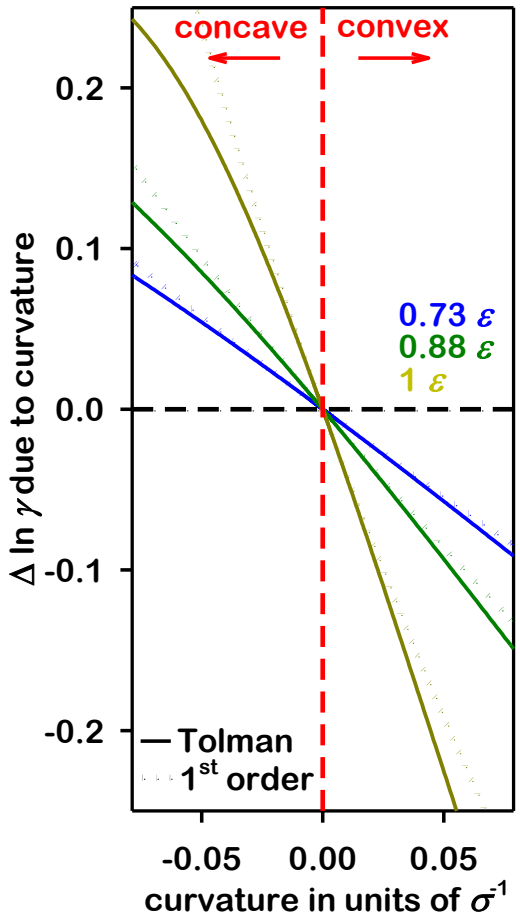
$$\frac{\gamma\, dR}{R\, d\gamma} = 1 + \left(\frac{\delta}{R} + \frac{\delta^2}{2R^2}\right)^{-1}$$

$$\frac{\gamma_0}{\gamma} \approx 1 + \frac{\delta_0}{R} + \frac{2\ell^2}{R^2}$$

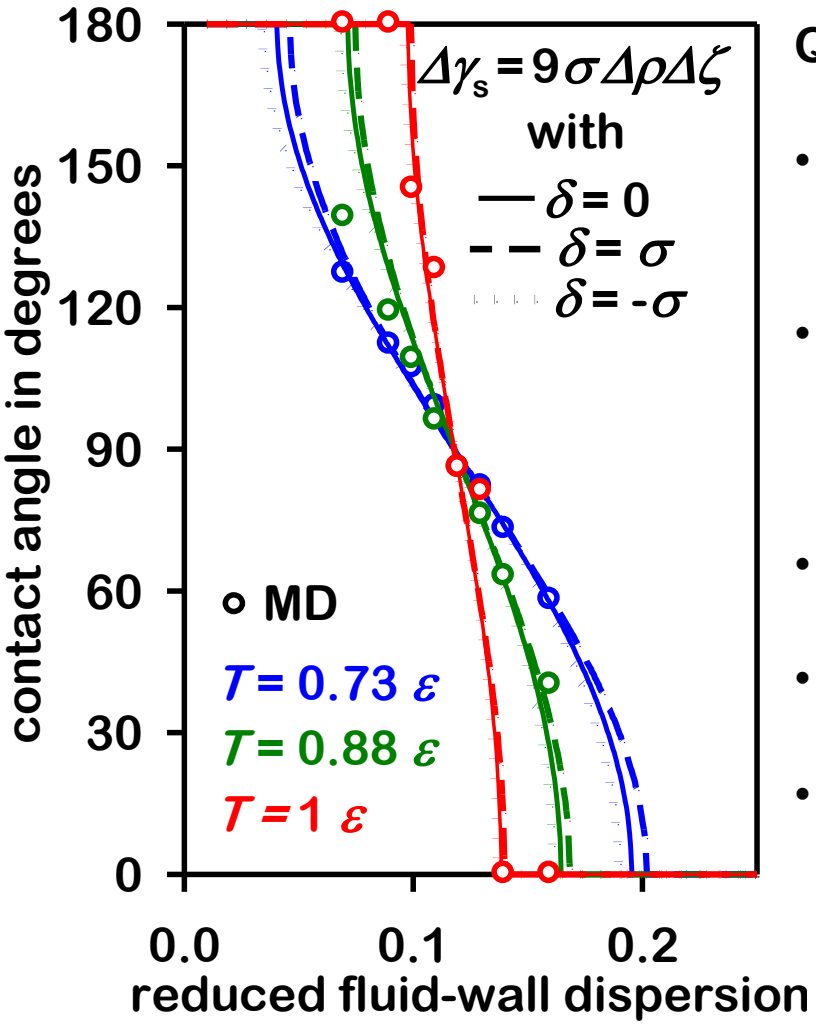
Young-Tolman

$$\cos\theta = \Delta\gamma_s/\gamma$$

$$\approx \left(\frac{\gamma_0}{\Delta\gamma_s} + \frac{2\delta_0}{h}\right)^{-1}$$



Tolman theory and cylindrical interfaces (III)



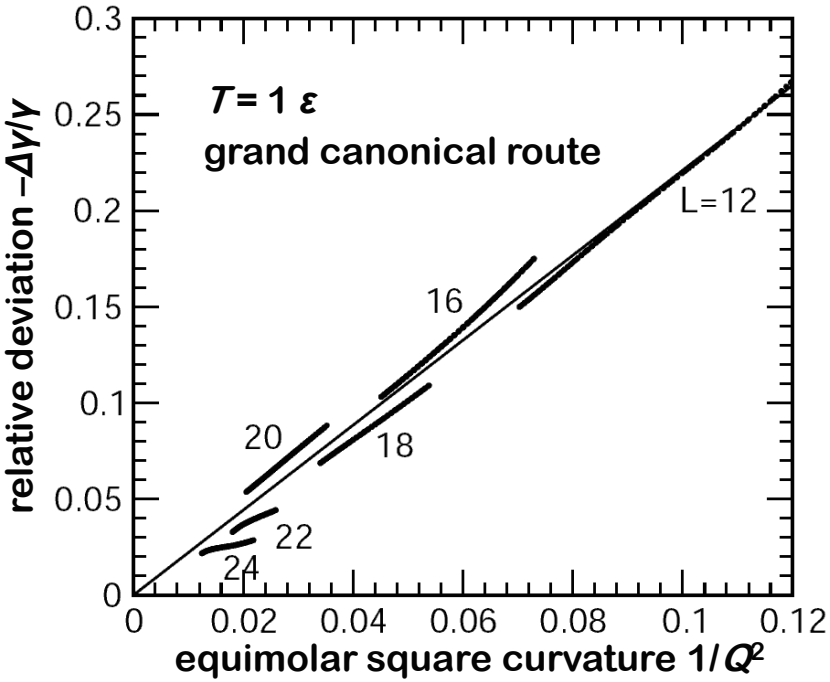
Qualitative observations:

- Only for a narrow range of ζ values there is a contact angle.
- For a temperature-independent magnitude of ζ, the contact angle becomes rectangular as $\Delta\gamma_s = 0$.
- First-order wetting transition.
- General tendency: $\Delta\gamma_s \sim \Delta\rho\Delta\zeta$.
- The curvature influence on θ is negligible at high temperatures.

Tolman theory and cylindrical interfaces (IV)

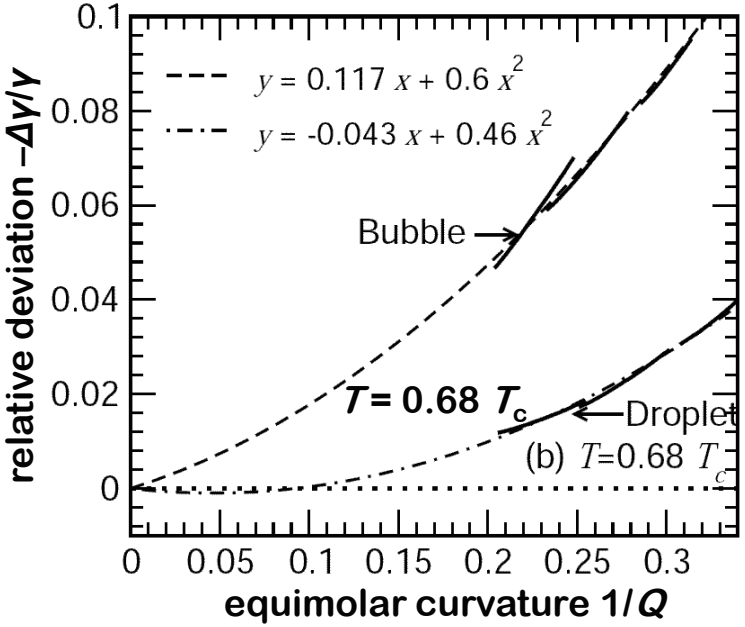
Cylindrical Tolman and Block length from MD simulation:

Symmetrical LJSTS liquid-liquid



Block length ℓ "close to" 1 σ

LJTS vapour-liquid ($r_c = 2^{7/6}\,\sigma$)



δ = -0.02 σ, ℓ = 0.3 σ

(Source: Block *et al.*, 2010)

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Analysis of spherical interfaces (I)

The variational route (TA method)

Canonical partition function:

$$\Delta F = -T \ln\left\langle \exp\left(-\frac{\Delta U}{T}\right)\right\rangle$$

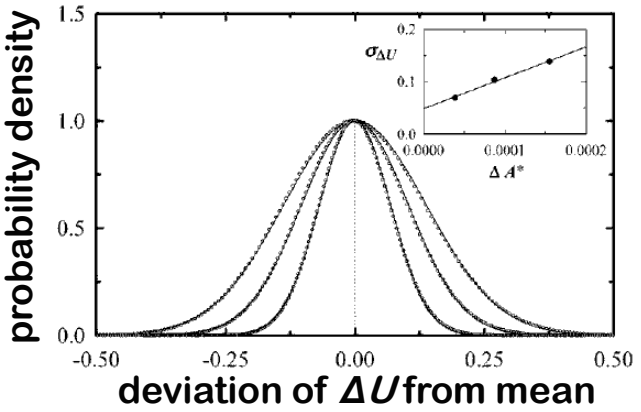
$$= f\left(\langle \Delta U\rangle, \langle \Delta U^2\rangle, \langle \Delta U^3\rangle\right) + O\left(\langle \Delta U^4\rangle\right)$$

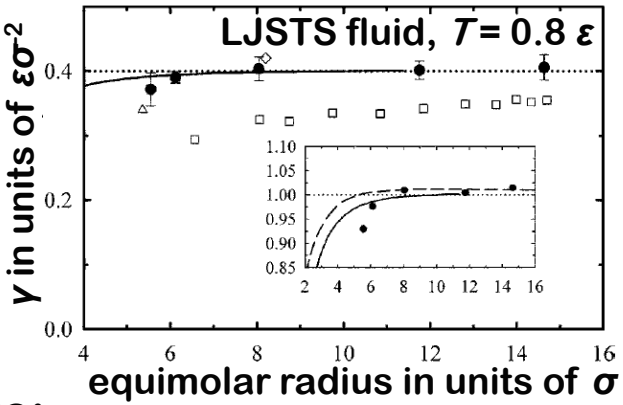
For small deformations:

$\gamma = \Delta F/\Delta A$ with $A = 4\pi Q^2 + O(\delta Q)$

Nonlinear terms are essential.

Tolman length much smaller than based on other methods.





(Source: Sampayo *et al.*, 2010)

Main advantages of the variational route:

- Free energy differences are considered in a direct way.
- No mechanical equilibrium assumption is applied.

Analysis of spherical interfaces (II)

The virial route

Bakker-Buff equation:

$$\gamma = R^{-2}\int_{\text{in}}^{\text{out}} dz\, z^2\left[p_{\text{N}}(z) - p_{\text{T}}(z)\right]$$

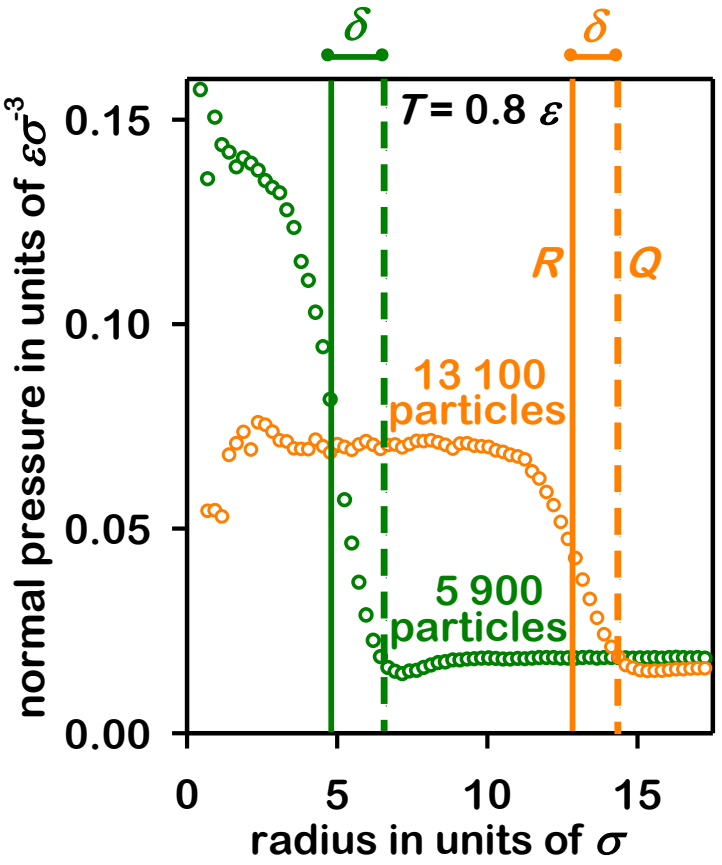
$$(2\gamma)^3 = -\Delta\rho^2 \int_{\text{in}}^{\text{out}} dp_{\text{N}}(z)\, z^3$$

Irving-Kirkwood pressure tensor:

$$p_{\text{N}}(z) = \sum_{\{i,j\}\in \mathbf{S}(z)} \frac{f_{ij}\left|\mathbf{s}\cdot\mathbf{r}_{ij}\right|}{4\pi z^3 r_{ij}} + kTp(z)$$

The p_{N} profile has a minimum.

In the vicinity of the surface of tension radius, p_{N} decays.



Main advantages of the virial route:

- Equilibrium sampling – no unstable states are considered.
- The Tolman length is obtained directly as $\delta = Q - R$.

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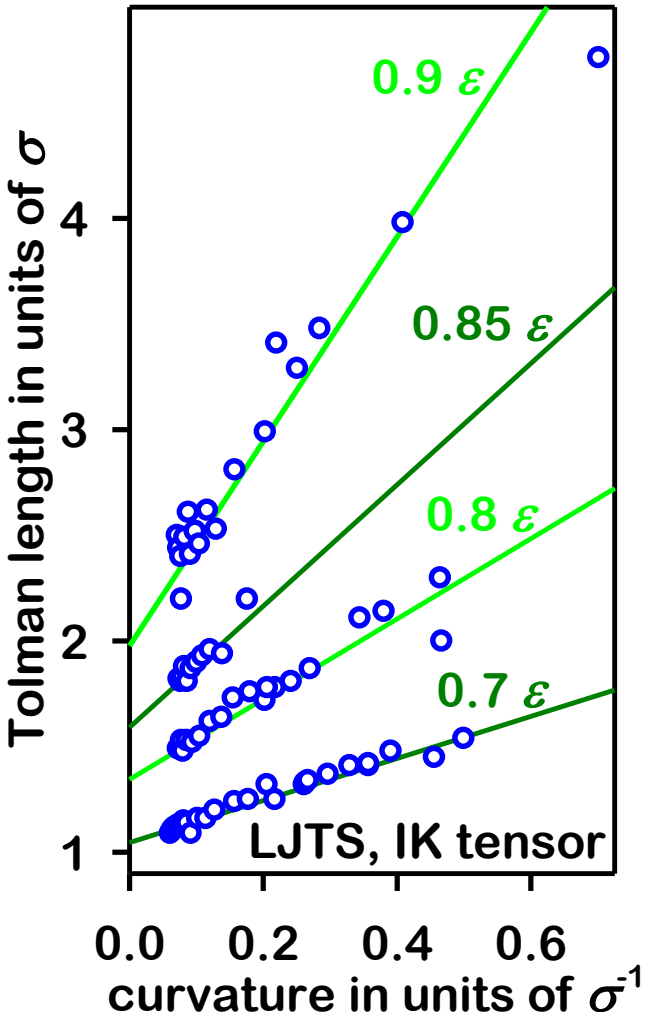
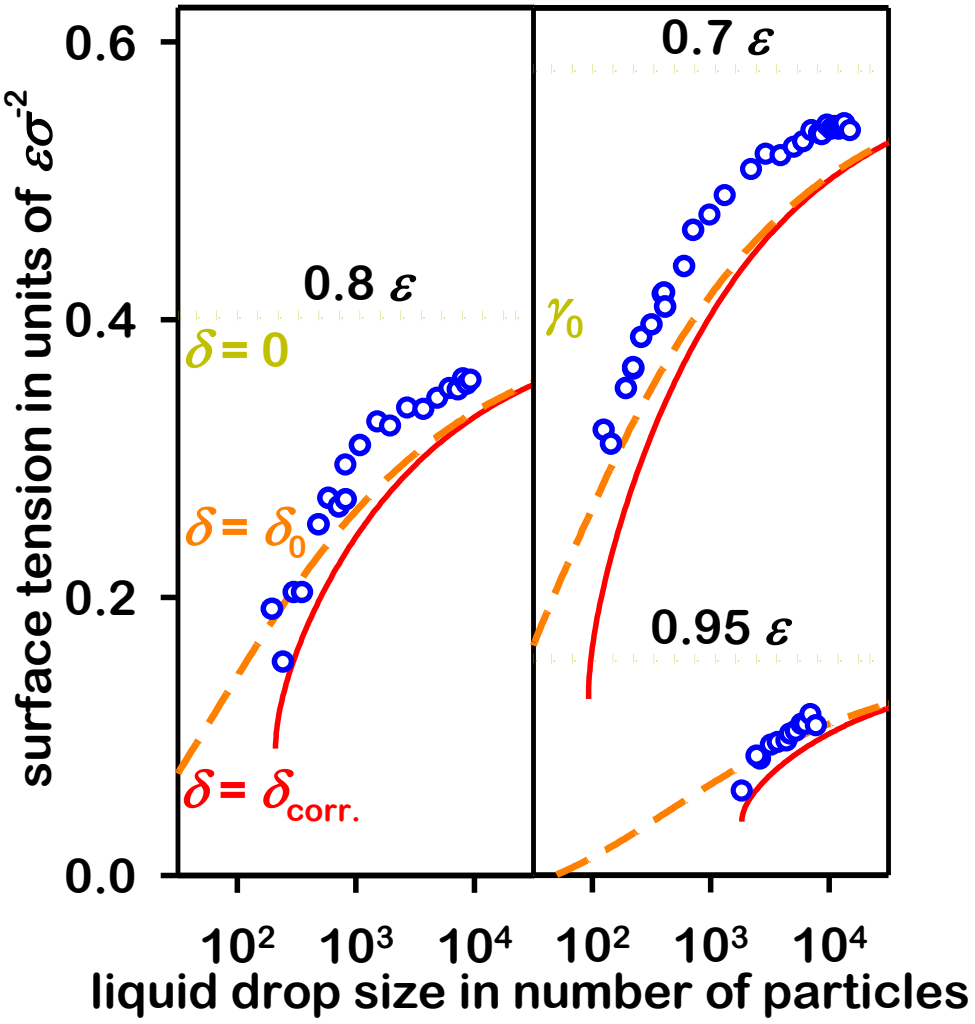
Analysis of spherical interfaces (III)





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Analysis of spherical interfaces (IV)

The grand canonical route

Excess Landau free energy:

$$\Sigma = \Omega(\rho) - \mu_{coex}(Q) \cdot \left[V'\rho'(Q) + V''\rho''(Q)\right]$$

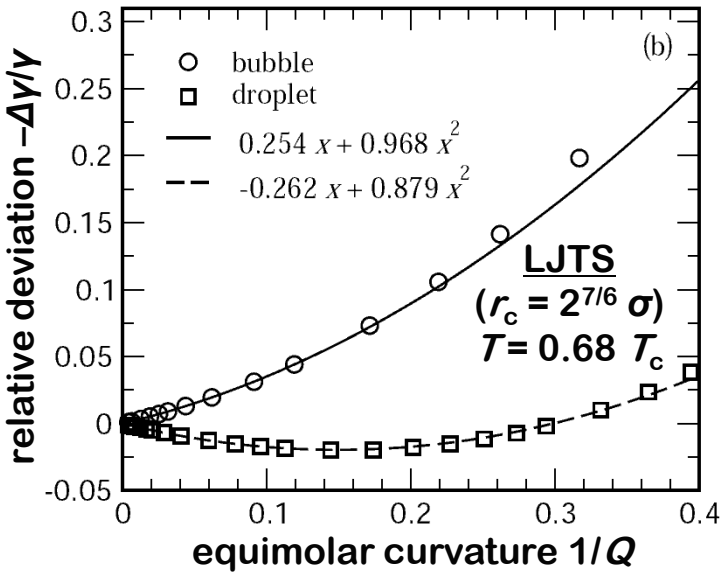
(from sampling of at μ, V, T const.)

Relation to the surface tension:

$$\Sigma = \int_0^{A(R)} \gamma dA = \hat{\gamma}\, 4\pi Q^2$$

The Tolman length is negative.

Contribution of the Block length causes the decay of γ.



(Source: Block *et al.*, 2010)

Main advantages of the grand canonical route:

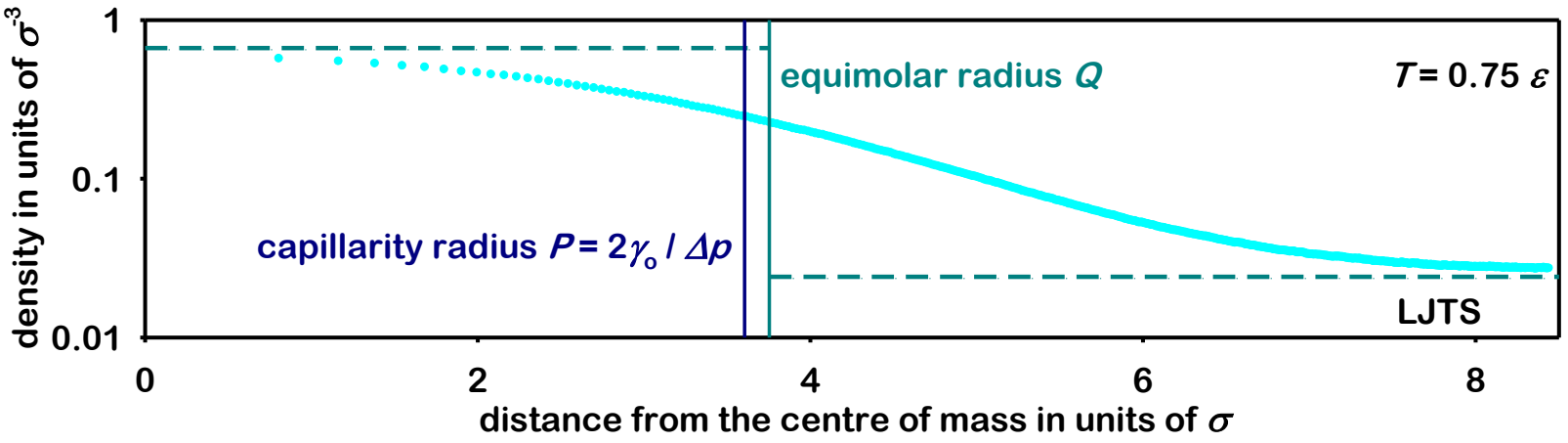
- A range of bubble/drop sizes is sampled at the same time.
- Leads to surface free energy (instead of surface tension).

The excess equimolar radius (I)

The standard Tolman approach is based on:

- The equimolar radius Q, related to the density profile.
- The surface of tension radius $R = 2\gamma/\Delta p$, related to γ.
- The dependence of γ on $1/R$, which is coupled to γ itself.

As long as $\gamma(R)$ is disputed, so are R and $\delta = Q - R$ as well …



Idea: use $\varphi(\mu, T) = \Delta p/2$ instead of $1/R$, and "replace" R by $P = \gamma_0/\varphi$.

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The excess equimolar radius (II)

Van Giessen-Blokhuis eqn.

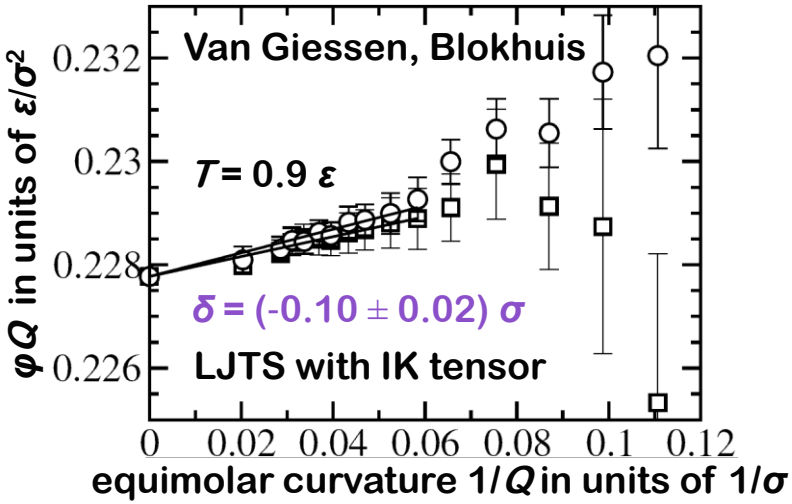
$$-\delta_0 = \frac{1}{\gamma_0}\left(\lim_{Q\to\infty} \frac{d}{d(1/Q)}\varphi Q\right)$$

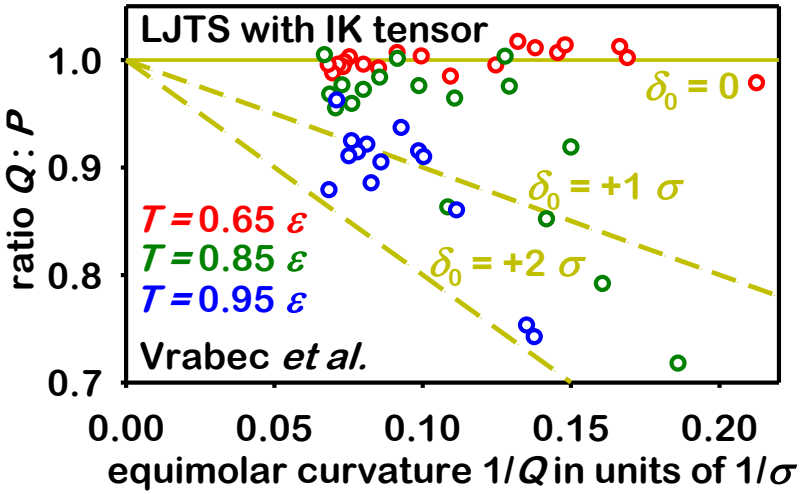
Equivalent expression for the zero-curvature Tolman length from the ratio between P and Q:

$$-\delta_0 = \lim_{1/Q\to 0} \frac{d}{d(1/Q)}\frac{Q}{P}$$

➡ Theory in terms of P and Q

Simulation studies using the IK pressure tensor come to contradictory conclusions.





The excess equimolar radius (III)

Tolman theory in *Q*, *R*, and *1/R*

Tolman length:

$$\delta = Q - R = Q - \frac{\gamma}{\varphi}$$

Full Tolman equation:

$$\frac{\gamma\, dR}{R\, d\gamma} = 1 + \left(\frac{2\delta}{R} + \frac{2\delta^2}{R^2} + \frac{2\delta^3}{3R^3} \right)^{-1}$$

First-order expansion:

$$\frac{\gamma_0}{\gamma} = 1 + \frac{2\delta_0}{R} + O\left(\frac{1}{R^2} \right)$$

Tolman theory in *P*, *Q*, and *φ*

Excess equimolar radius:

$$\eta = Q - P = Q - \frac{\gamma_0}{\varphi}$$

Full Tolman equation:

$$\frac{\varphi\, d\gamma}{\gamma\, d\varphi} = \frac{2}{3}\left(1 - \left[\frac{\eta\varphi + \gamma_0}{\gamma} \right]^3 \right)$$

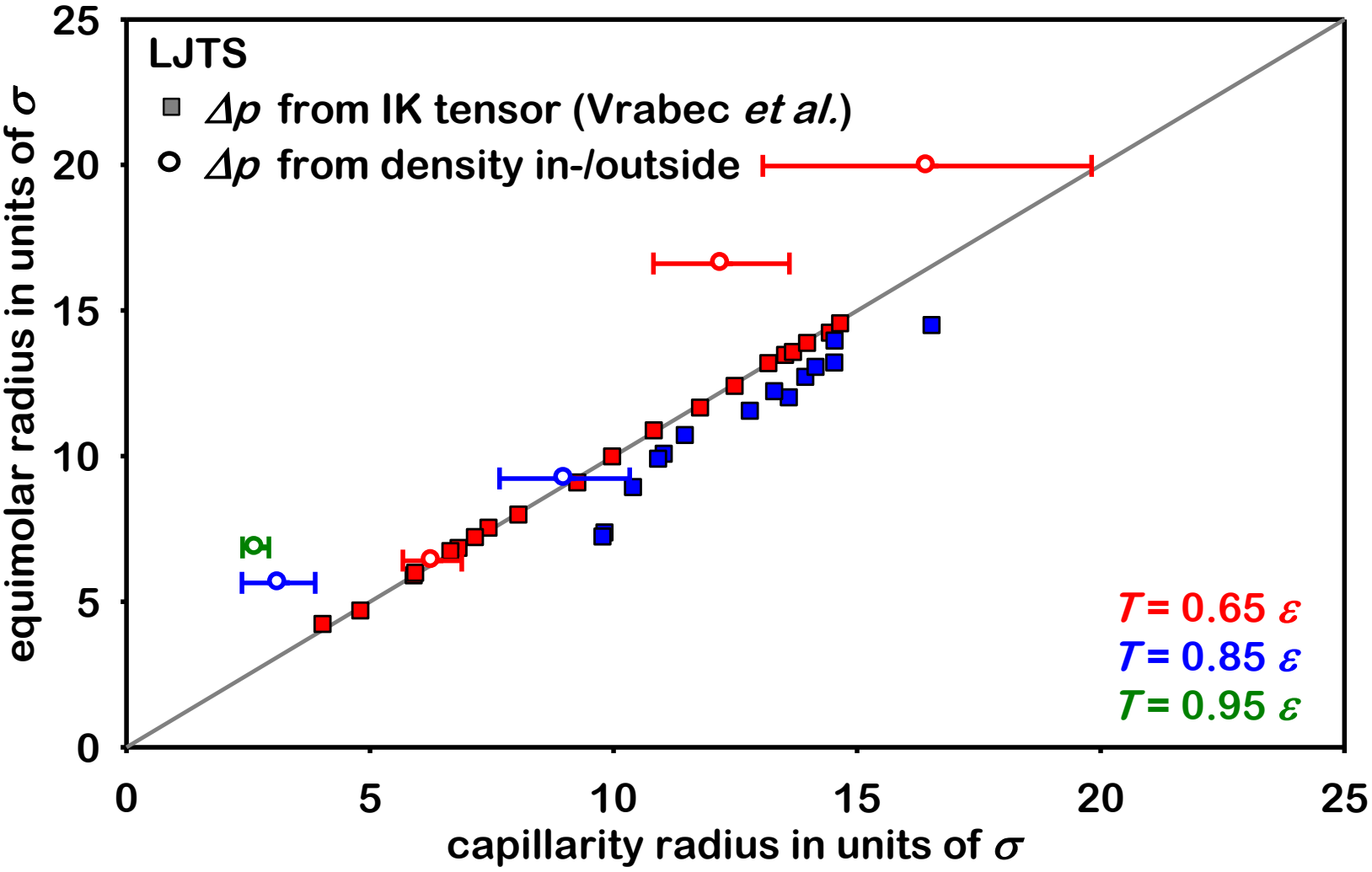
First-order expansion:

$$\gamma = \gamma_0 + 2\eta_0\varphi + O\left(\varphi^2\right)$$

How do these notations relate to each other?

$$\eta_0 = \lim_{\varphi \to 0}\left(Q - \frac{\gamma_0}{\varphi} \right) = -\lim_{R \to \infty}\left(Q - \frac{\gamma}{\varphi} \right) = -\delta_0$$

The excess equimolar radius (IV)



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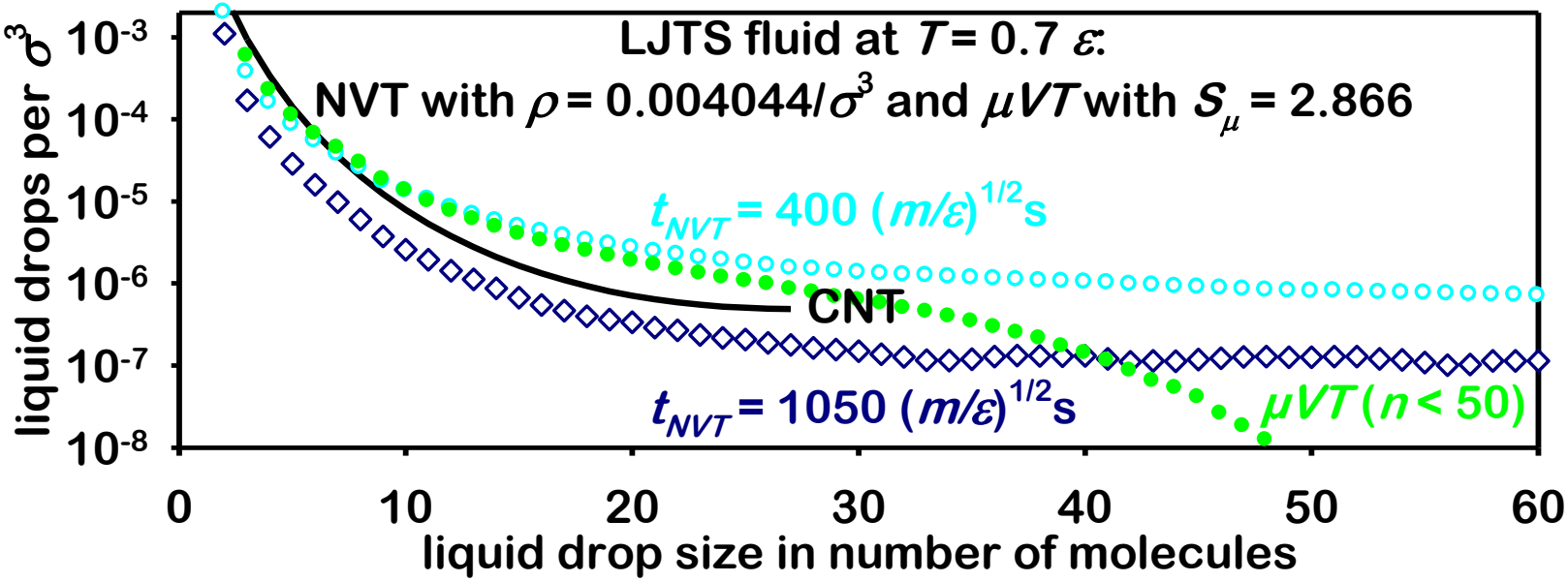
Correction of the classical nucleation theory (I)

Free energy of formation from simulation vs. CNT prediction:



But (almost) everybody agrees that $\gamma(R) \to 0$ for $R \to 0$ …

Deviation for γ ⟺ Agreement for n^*, J, and $\Delta F_n = \int_0^n \gamma dA$

Could it be that the surface area is larger than CNT assumes?

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Correction of the classical nucleation theory (II)

Equilibrium condition for critical droplets yields:

$2\,dV = R\,dA$ interpretation $dA = \frac{2dV}{R} \approx \frac{8\pi Q^2}{Q-\delta} dQ$

This postulate implies:

δ positive

↓

γ smaller than γ_0

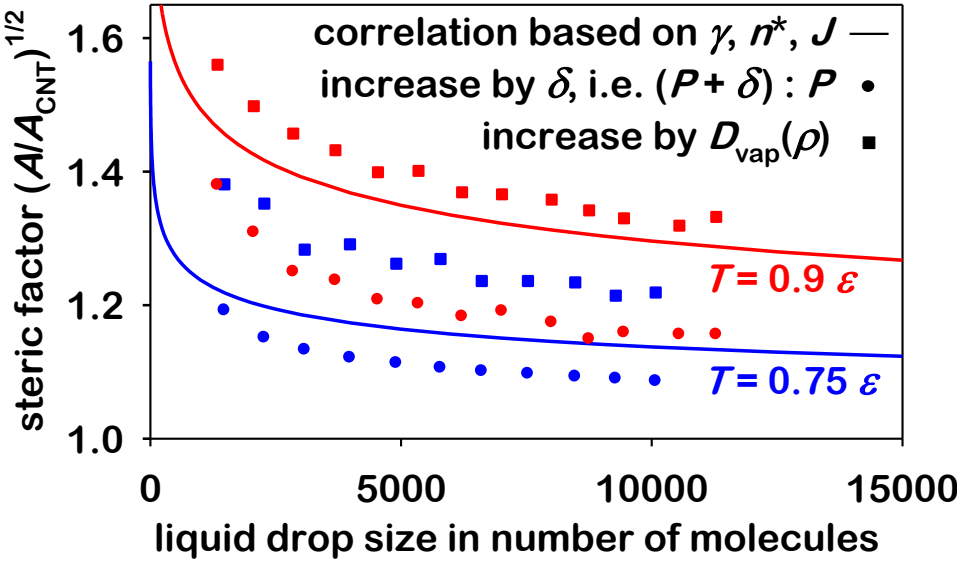
↓

A greater than $4\pi Q^2$

↓

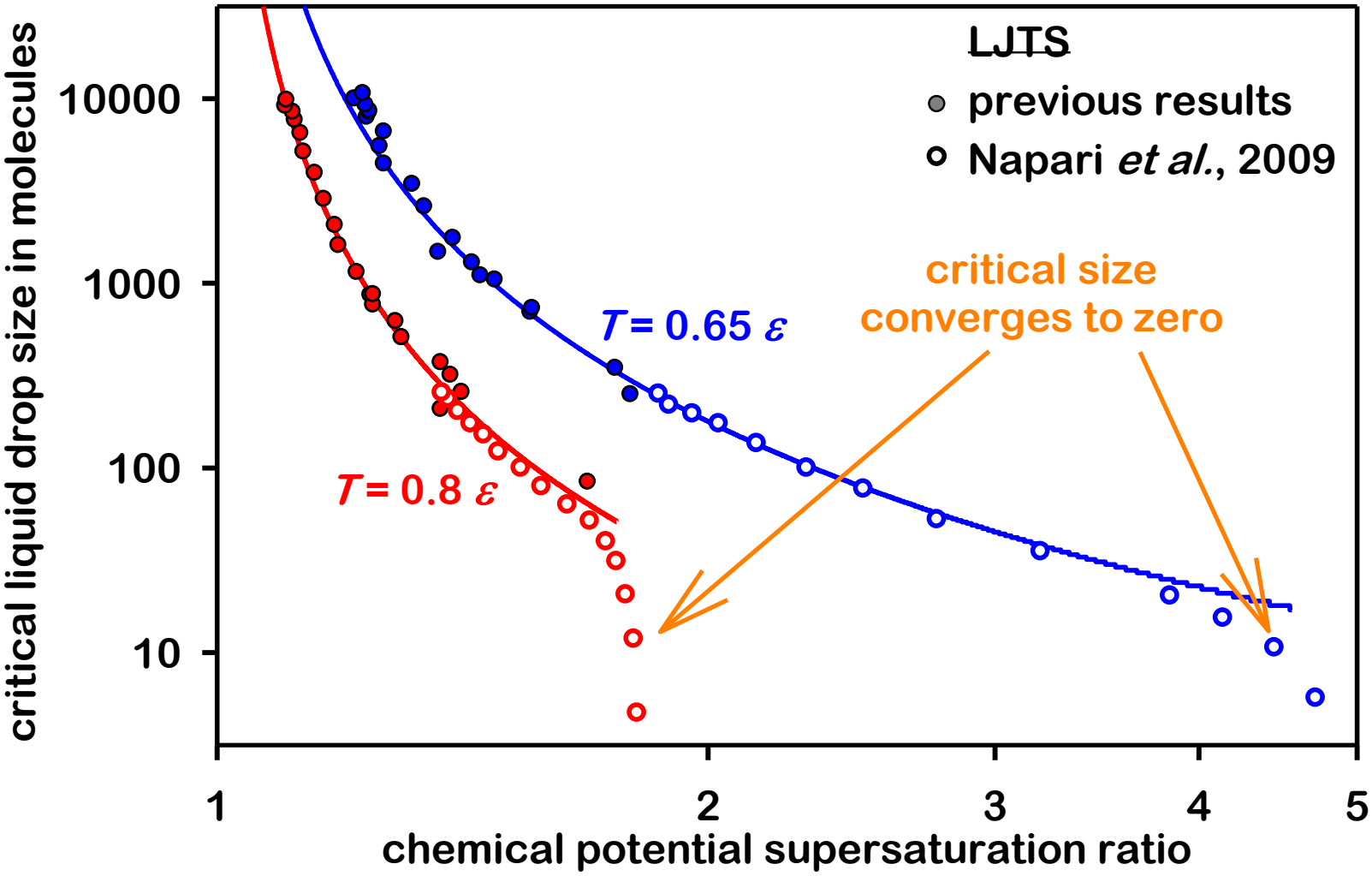
ΔF_n, n^*, and J similar

(and vice versa)



Phys. Rev. E **78**: 011603 (2008)

Correction of the classical nucleation theory (III)



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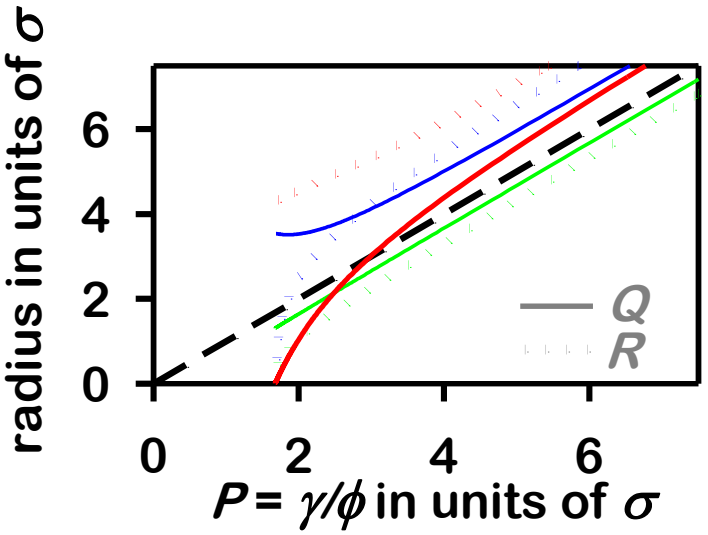
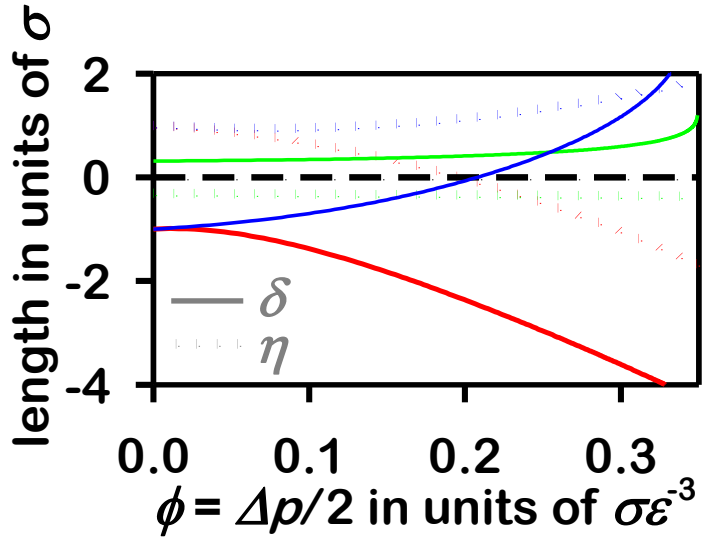
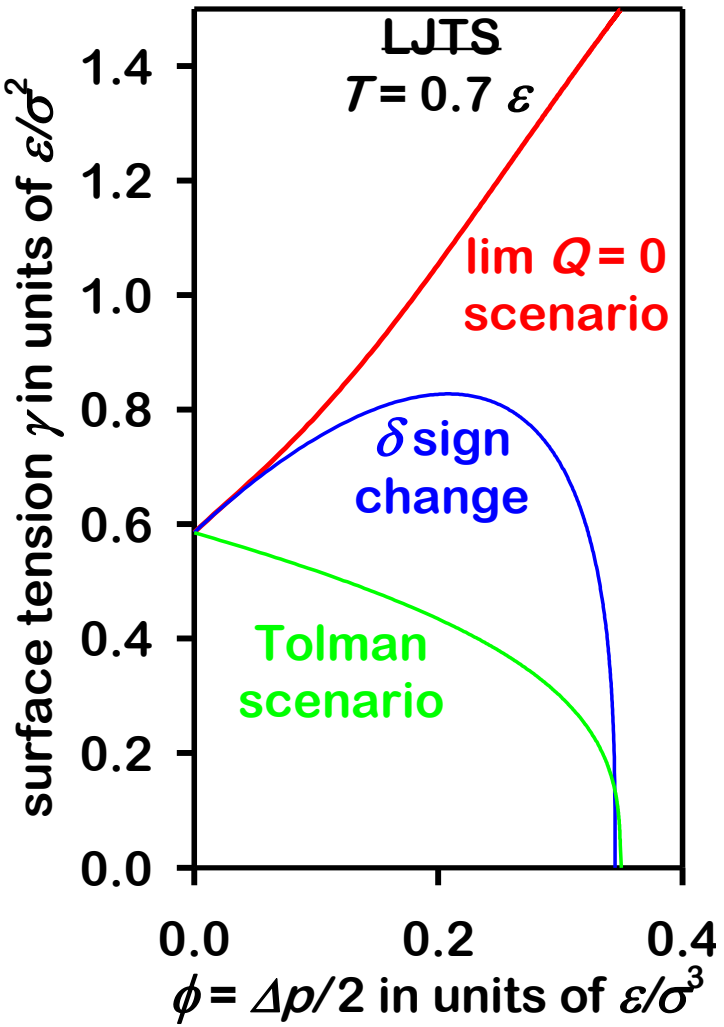
Correction of the classical nucleation theory (IV)







Conclusion

I know that I know nothing.

We must move beyond contradictory results and huge error bars.

This is surely possible.