Nucleation of multicomponent droplets

(with an application to vodka)

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August 30, 2019
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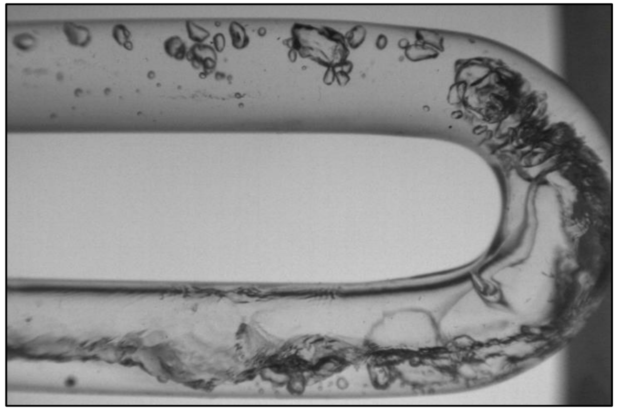
What is nucleation?

- The initial step in a phase transition
- Fluctuations in metastable phase → embryos of stable phase
- Nucleation theory tries to answer two questions
  1. **What are the properties of the embryos?**
  2. **What is the nucleation rate?**

$$J = \frac{\text{number of nucleated droplets}}{\text{time} \times \text{volume}}$$

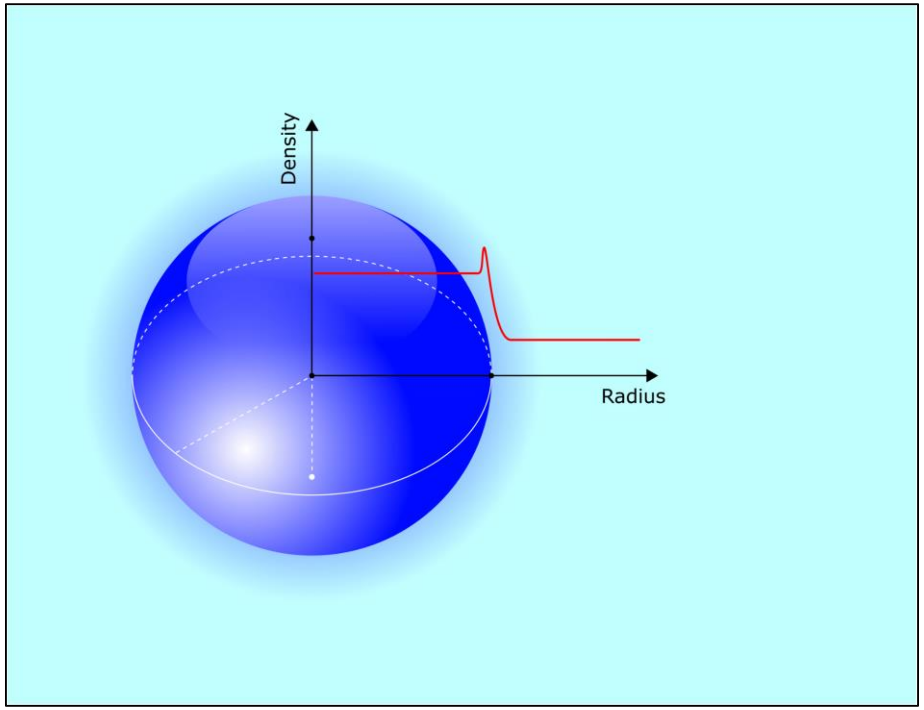
(nucleation rate)

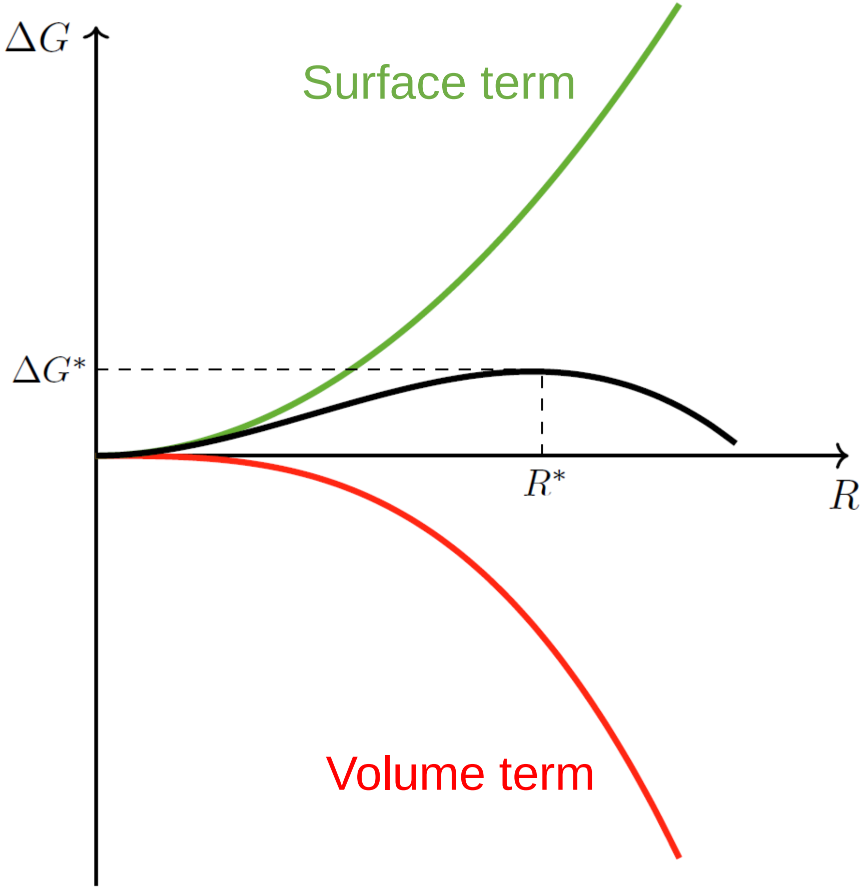


Classical Nucleation Theory (CNT)

The Classical Nucleation Theory

- Fluctuation theory: $\mathrm{Prob}(\mathrm{droplet}) \sim \exp\left(-\Delta G/kT\right)$
  - Free energy of liquid: described by bulk thermodynamics
  - Free energy of surface: described by surface tension





The Classical Nucleation Theory

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  - Free energy of liquid: described by bulk thermodynamics
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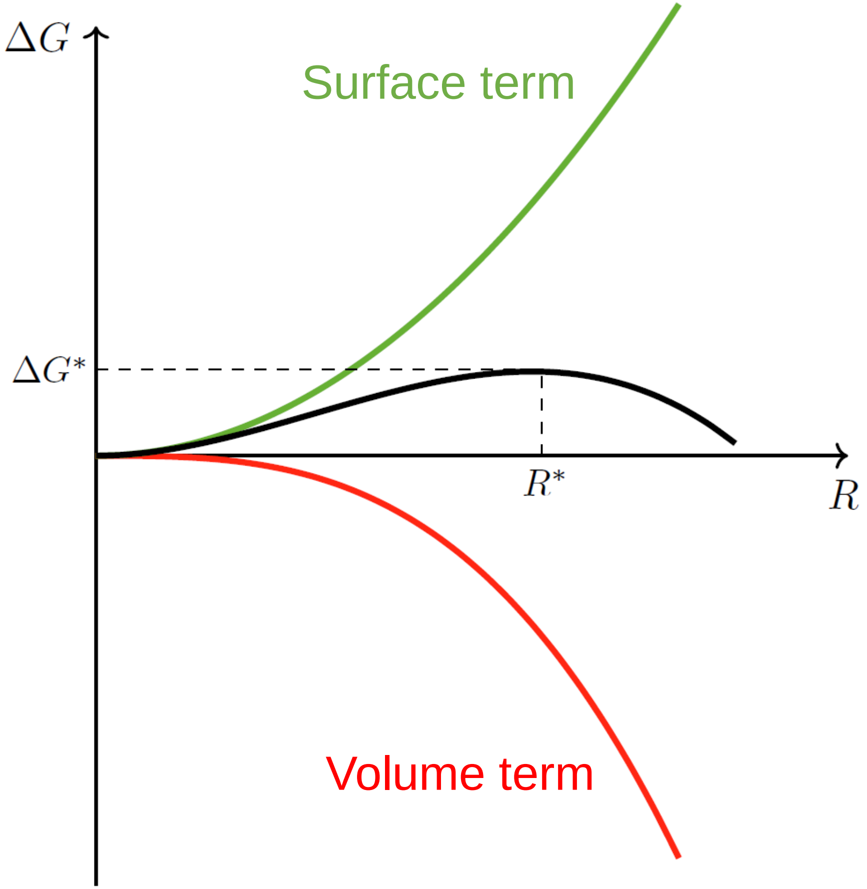
- CNT yields the predictions

$$\Delta G^* = 4\pi(R^*)^2\sigma^*/3$$

$$J_{\mathrm{CNT}} = K\exp\left(-\Delta G^*/kT\right)$$

- A key approximation:
  - Surface tension is independent of curvature

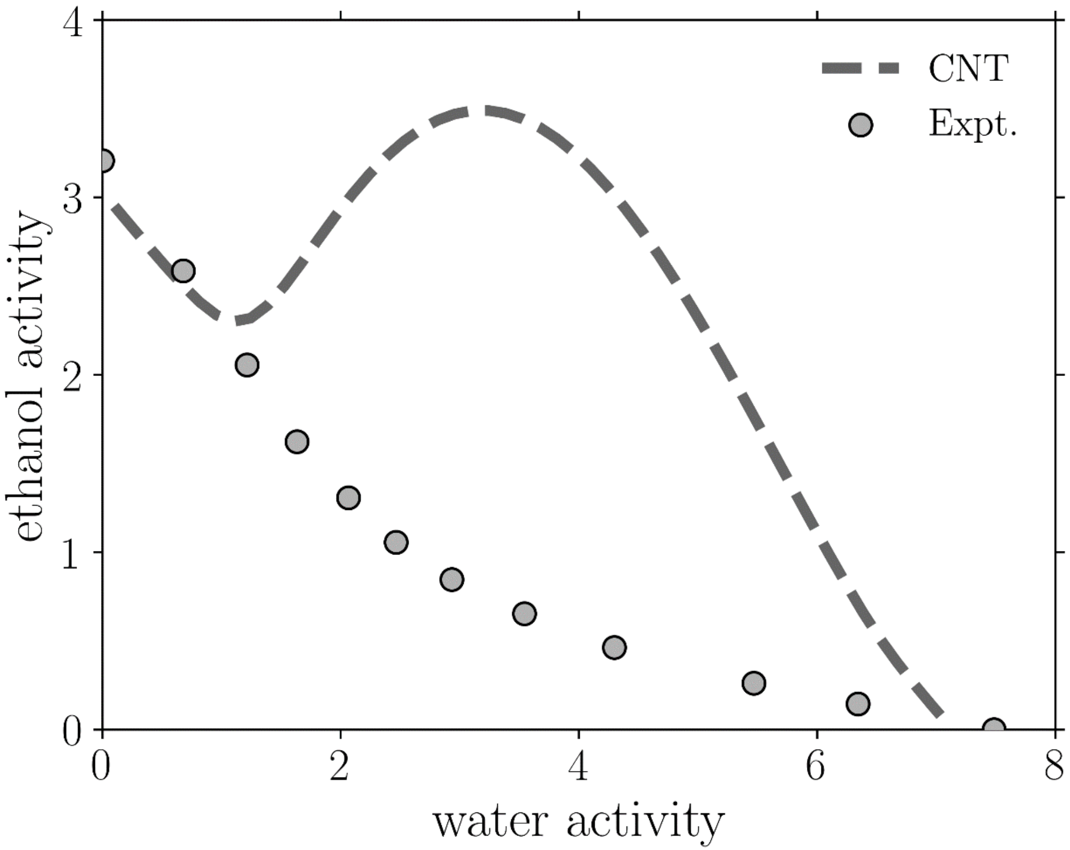


Performance of CNT

- Qualitatively reasonable picture of nucleation
- Quantitative errors are in some cases HUGE
  - Pure Ar nucleation rates underpredicted by ~20 orders of magnitude[1]
- Unphysical predictions for surface-active systems
  - Water-ethanol is particularly difficult

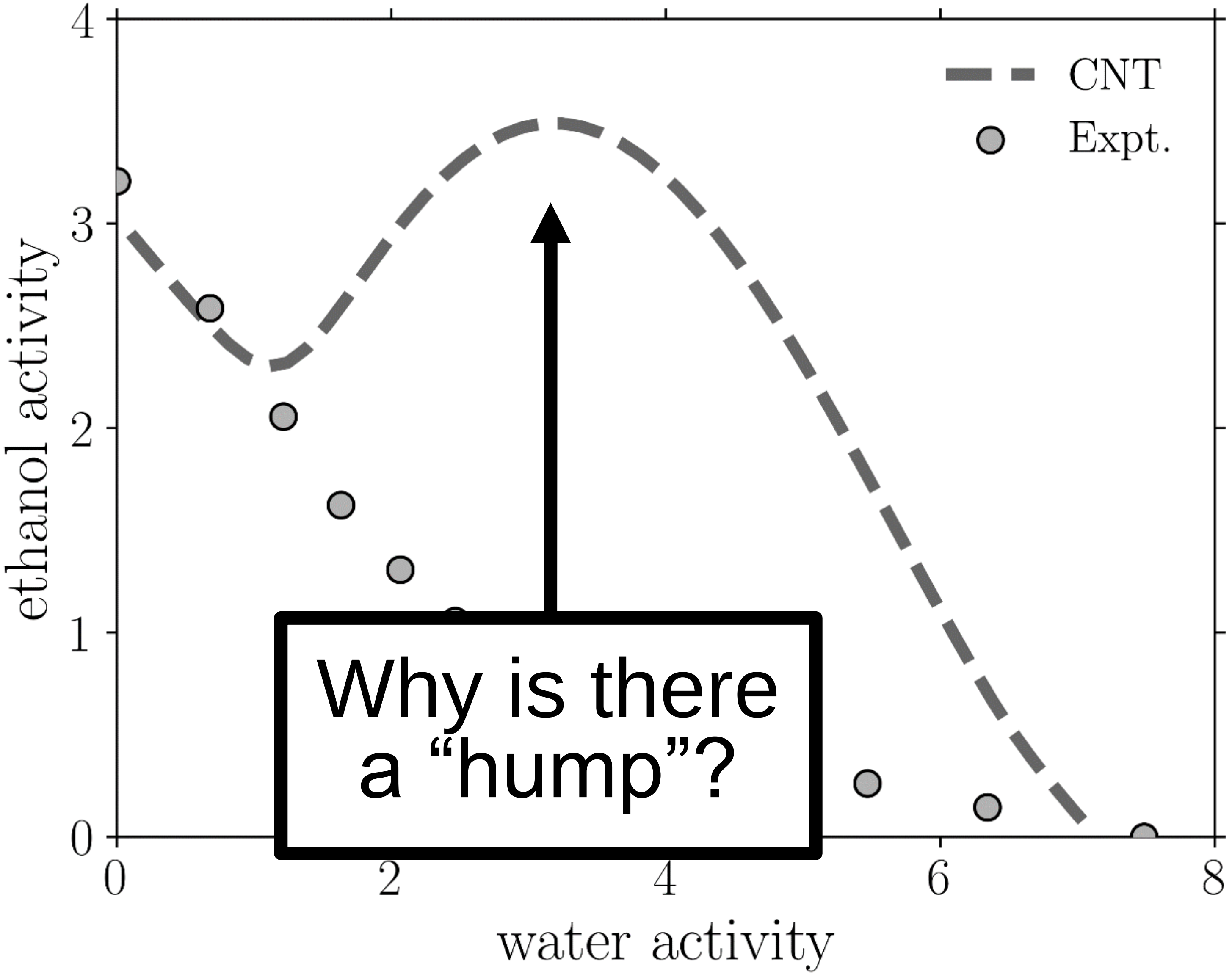
[1] Iland et al. 2007. Argon nucleation in a cryogenic nucleation pulse chamber. J. Chem. Phys.**127**

Critical activities of ethanol-water at 260 K



- Activities: $a_i = P_i/P_i^{\mathrm{sat}}$
- $J_{\mathrm{CNT}} = J_{\mathrm{CNT}}(a_1, a_2, T)$
- Critical activities:

$$J_{\mathrm{spec}} = 10^{13}\ \mathrm{m}^{-3}\mathrm{s}^{-1}$$



Why is there a “hump”?

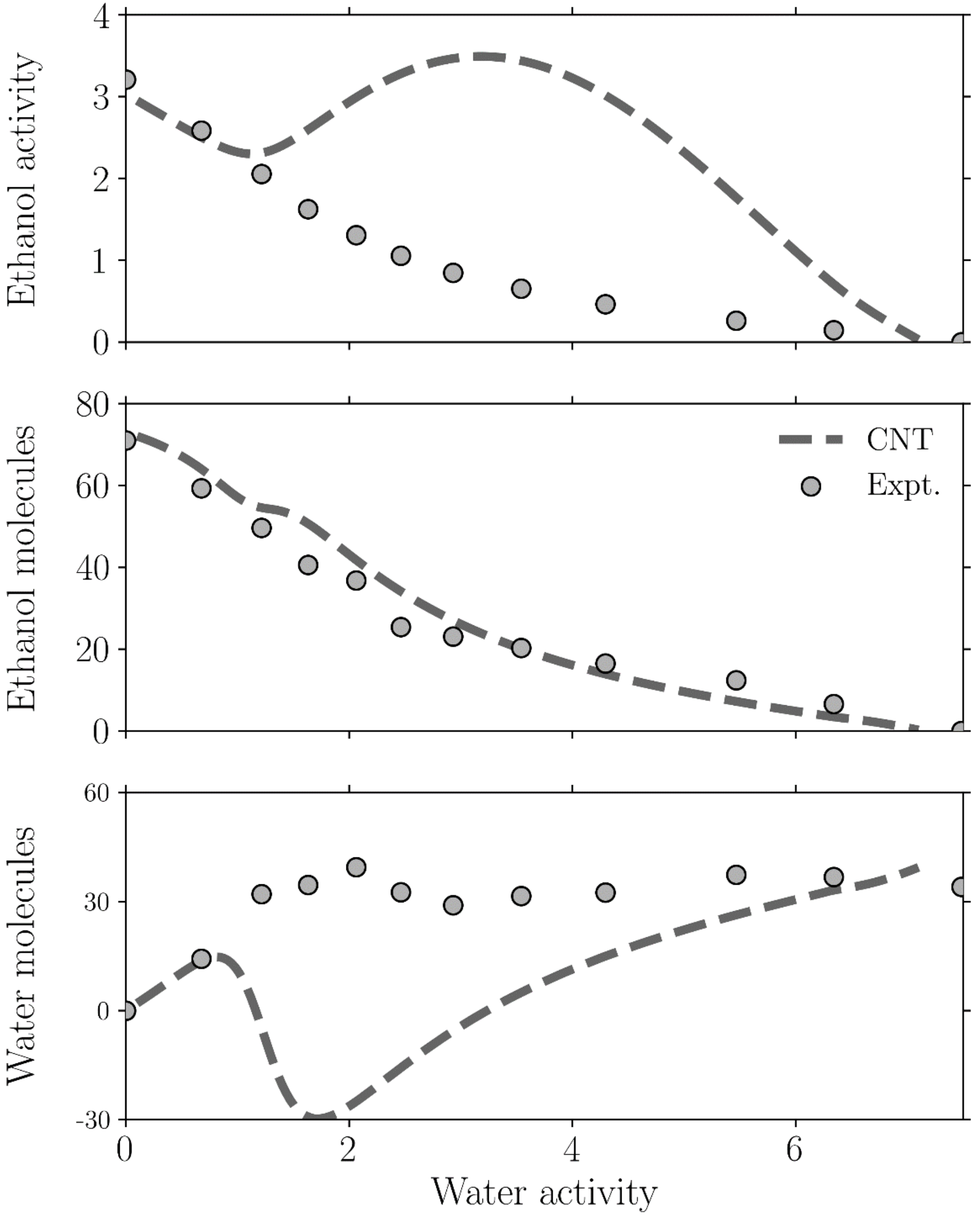
Why is there a “hump”?

- Result from nucleation theory:

$$\left(\frac{\partial a_2}{\partial a_1}\right)_{J,T} = -\frac{a_2}{a_1}\frac{N_1}{N_2}$$

- CNT predicts a **negative** amount of water particles in the critical droplet!

- Completely unphysical



A well-known problem

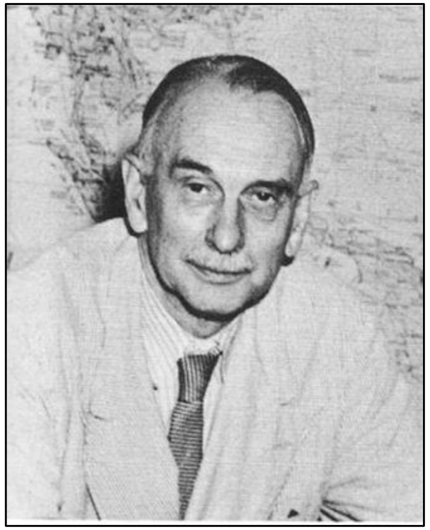
- *Unfortunately the water-ethanol system is so strongly surface active that classical theory breaks down…*[1]

- *Surface enrichment of ethanol in the clusters […] is presumably the origin of the observed discrepancy.*[2]

[1] Vehkamäki. Classical nucleation theory for multicomponent systems. Springer 2006.
[2] Viisanen et al. 1994. Measurement of the molecular content of binary nuclei. II. Use of the nucleation rate surface for water-ethanol. J. Chem. Phys. **100**.

Curvature-corrected CNT (c-CNT)

Curvature-dependent surface tension



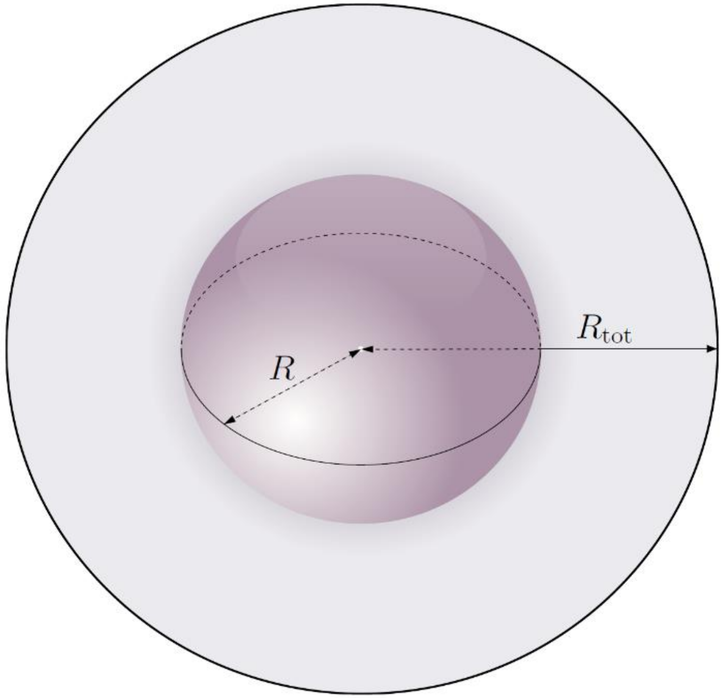
- Historically a controversial topic[1,2]
- Pure fluids
  - Emerging consensus on the curvature dependence
  - Dramatic improvement for pure water nucleation[3]
- Mixtures
  - Barely treated in the literature
  - Only recently proposed and calculated[4]

[1] Tolman 1949. The effect of droplet size on surface tension. J. Chem. Phys. **17**.
[2] Malijevský and Jackson 2012. A perspective on the interfacial properties of nanoscopic drops. J. Phys.: Condens. Matter **24.**
[3] Wilhelmsen et al. 2015. The Tolman length and ridigity constants of water and their role in nucleation. J. Chem. Phys. **142**.
[4] Aasen et al. 2018. Tolman lengths and rigidity constants of multicomponent fluids: Fundamental theory and numerical examples. J. Chem. Phys. **148**.

Curvature-dependent surface tension – pure fluids

The capillary approximation

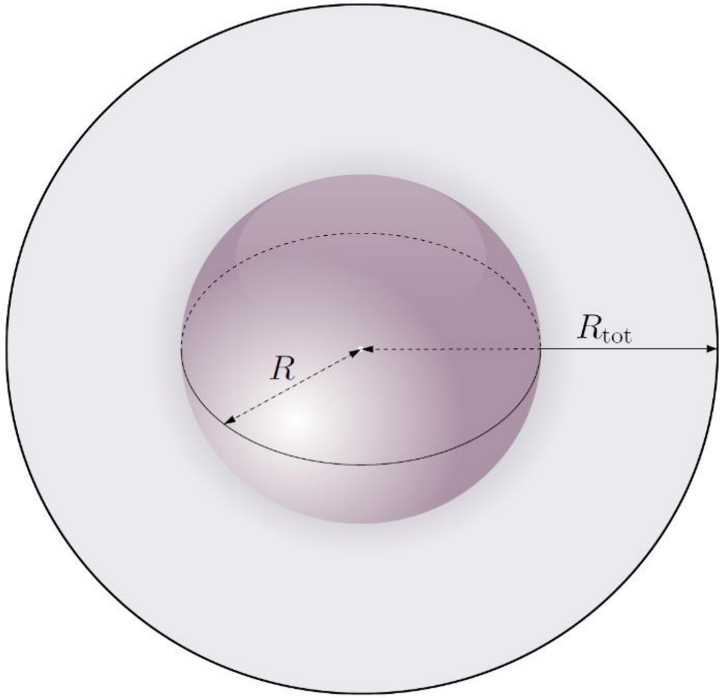
$$\sigma(R) = \sigma_0$$



Curvature-dependent surface tension – pure fluids

The Helfrich expansion

$$\sigma(R) = \sigma_0 + \frac{\sigma_1}{R} + \frac{\sigma_2}{R^2}$$



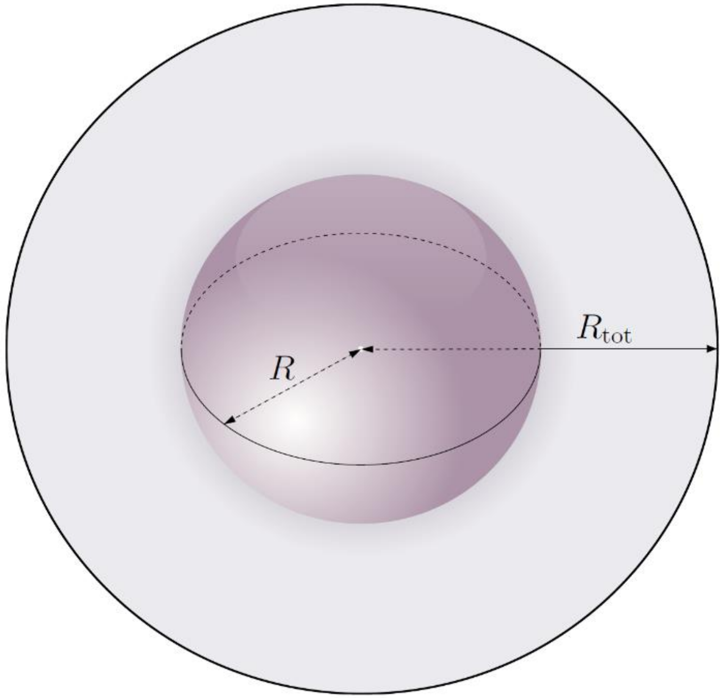
Helfrich coefficients:

- $\sigma_1 = -2\sigma_0\delta$, where δ is the **Tolman length**
- $\sigma_2 = 2k + \bar{k}$, where $k, \ \bar{k}$ are **rigidity constants**

Curvature-dependent surface tension – mixtures

The capillary approximation

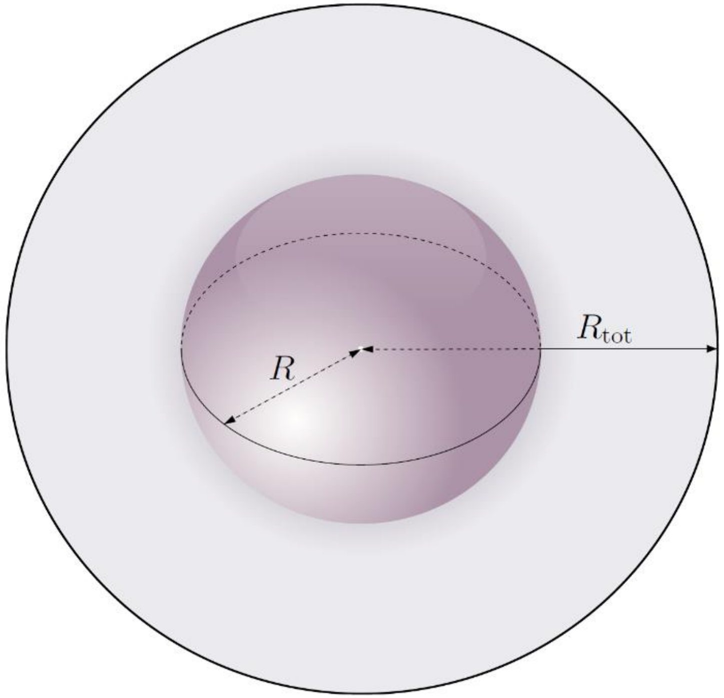
$$\sigma(R, \boldsymbol{x}) = \sigma_0(\boldsymbol{x})$$



Curvature-dependent surface tension – mixtures

The Helfrich expansion

$$\sigma(R, \boldsymbol{x}) = \sigma_0(\boldsymbol{x}) + \frac{\sigma_1(\boldsymbol{x})}{R} + \frac{\sigma_2(\boldsymbol{x})}{R^2}$$

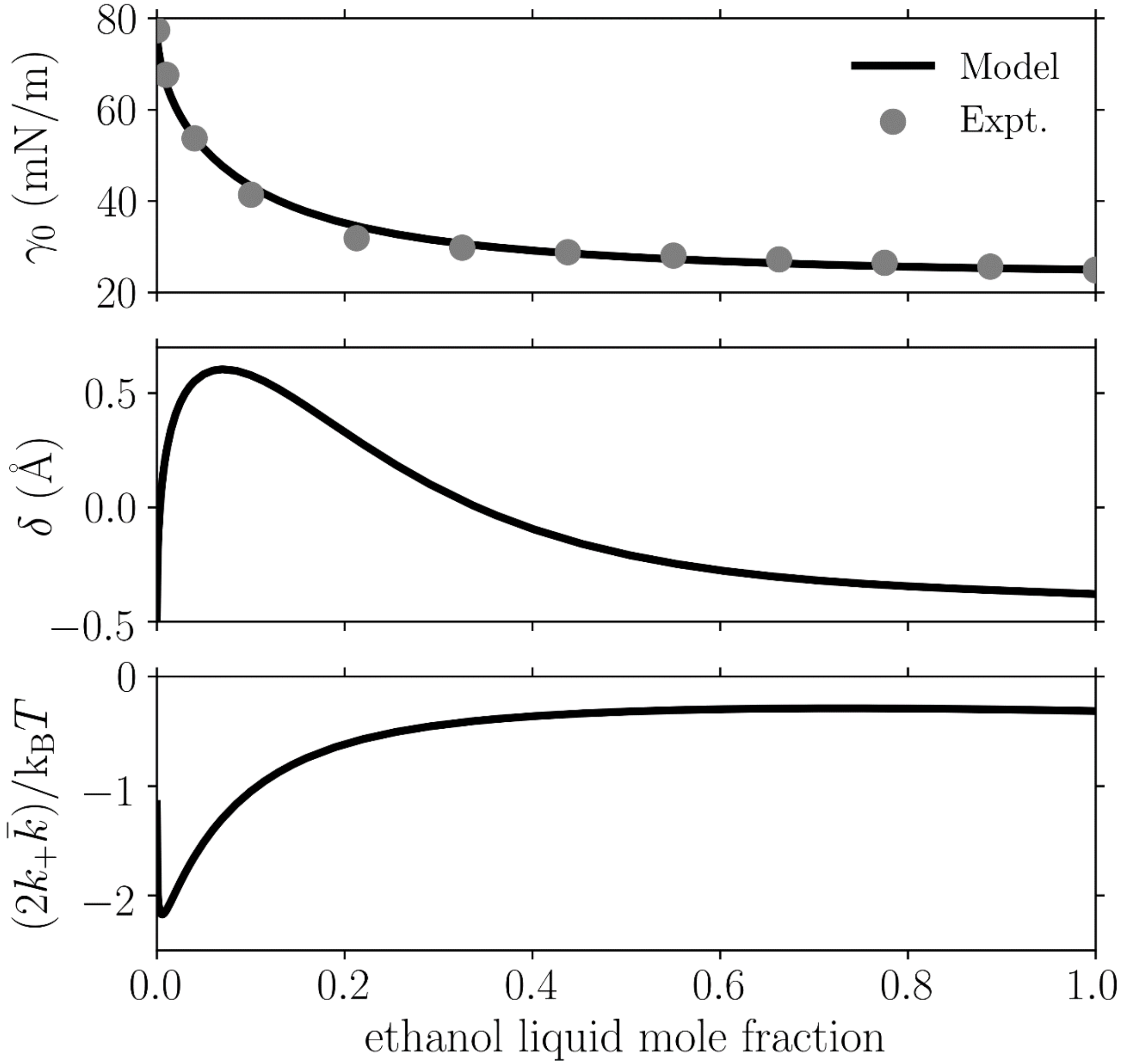


Helfrich coefficients:

- $\sigma_1 = -2\sigma_0\delta$, where δ is a **mixture Tolman length**
- $\sigma_2 = 2k + \bar{k}$, where $k,\ \bar{k}$ are **mixture rigidity constants**

Helfrich coefficients

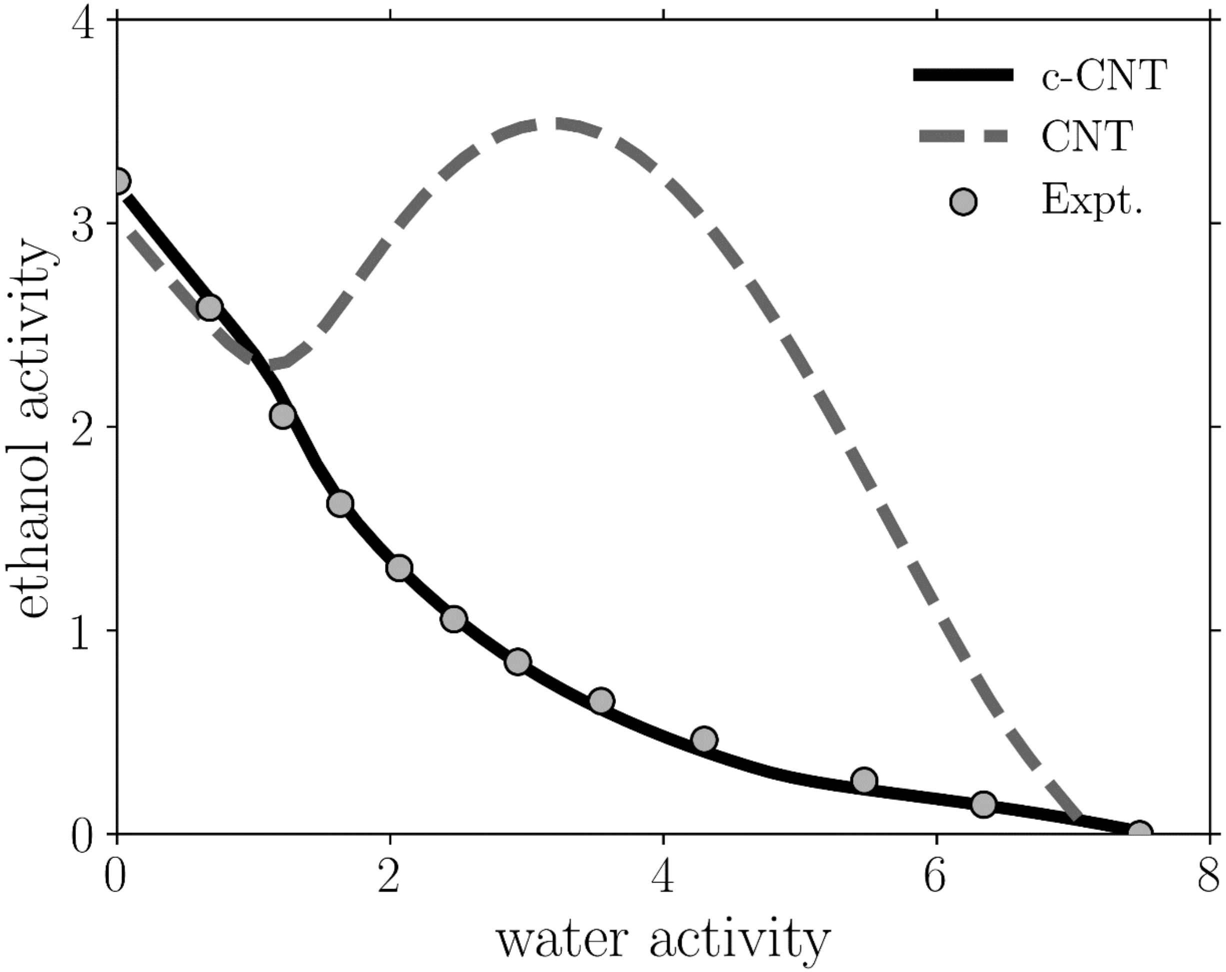
- Computed using Density Gradient Theory[1]
    - CPA equation of state for bulk thermodynamics
    - Fit to planar surface tension for ethanol and water
- No fitting to nucleation experiments



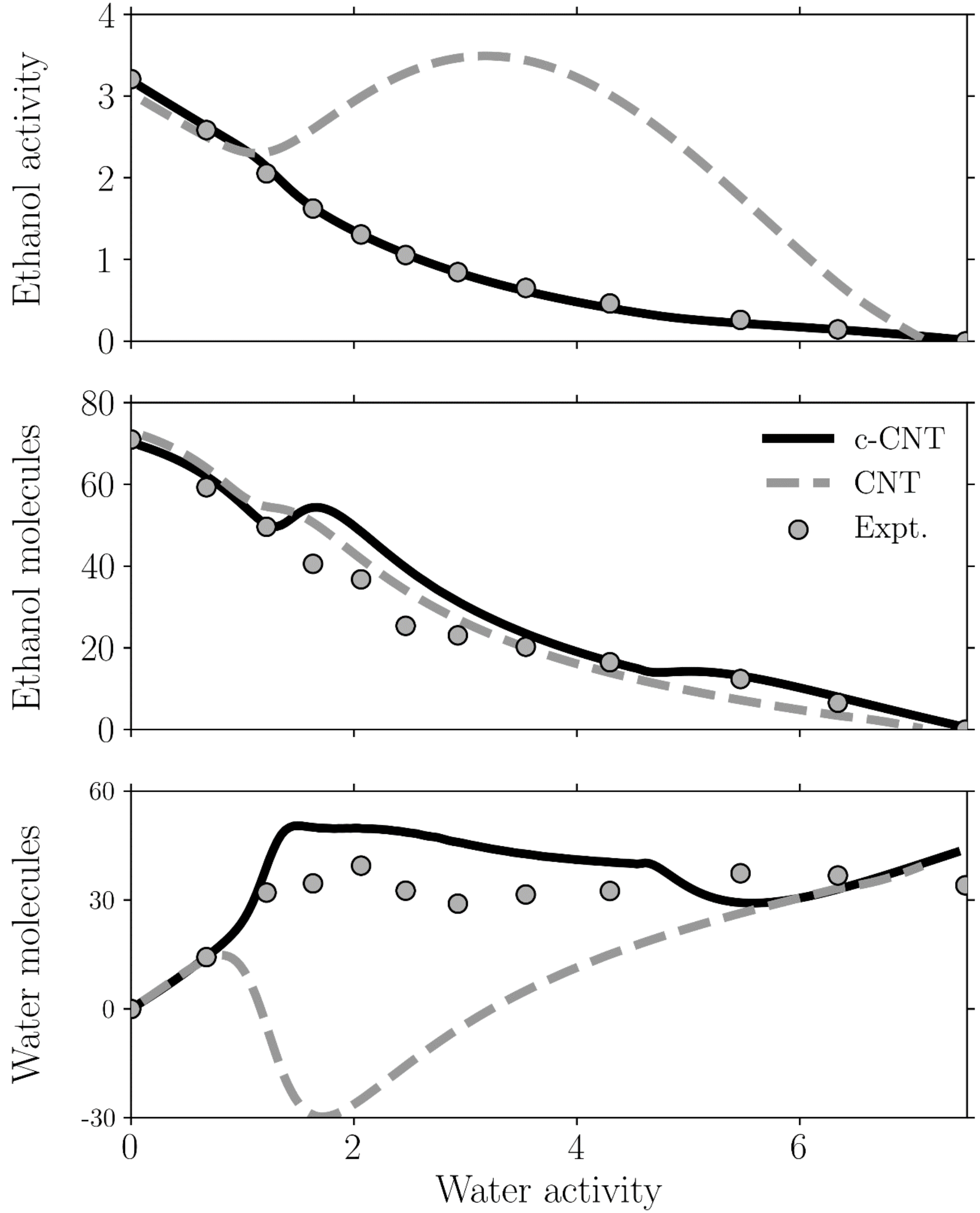
[1] Aasen et al. 2018. Tolman lengths and rigidity constants of multicomponent fluids: Fundamental theory and numerical examples. J. Chem. Phys. **148**.

Comparison of CNT and c-CNT

Critical activities: c-CNT vs. experiments



Molecular content: c-CNT vs. experiments



Quantitative improvement for the rates

- Measure of deviation: $\left|\log_{10}\left(J/J_{\mathrm{expt}}\right)\right|$
- Measurements[1] at 260 K for ethanol-water

	CNT	c-CNT
Worst	21.3	2.23
Average	10.9	0.73
Median	12.7	0.51

[1] Viisanen et al. 1994. Measurement of the molecular content of binary nuclei. II. Use of the nucleation rate surface for water-ethanol. J. Chem. Phys. **100**.

Concluding remarks

- Problems of CNT:
  - J_{CNT} can be quantitatively wrong by ~20 orders of magnitude
  - Predicts unphysical molecular content of critical clusters

- Helfrich coefficients can be computed from an independent model, and incorporated consistently into the theory $\rightarrow$ c-CNT

- c-CNT yields quantitative agreement with experiment

Thank you

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