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Confinement effects in heterogeneous nucleation of droplets on solid particles

A.K. Shchekin, L.A. Gosteva, T.S. Lebedeva, D.V. Tatyanenko

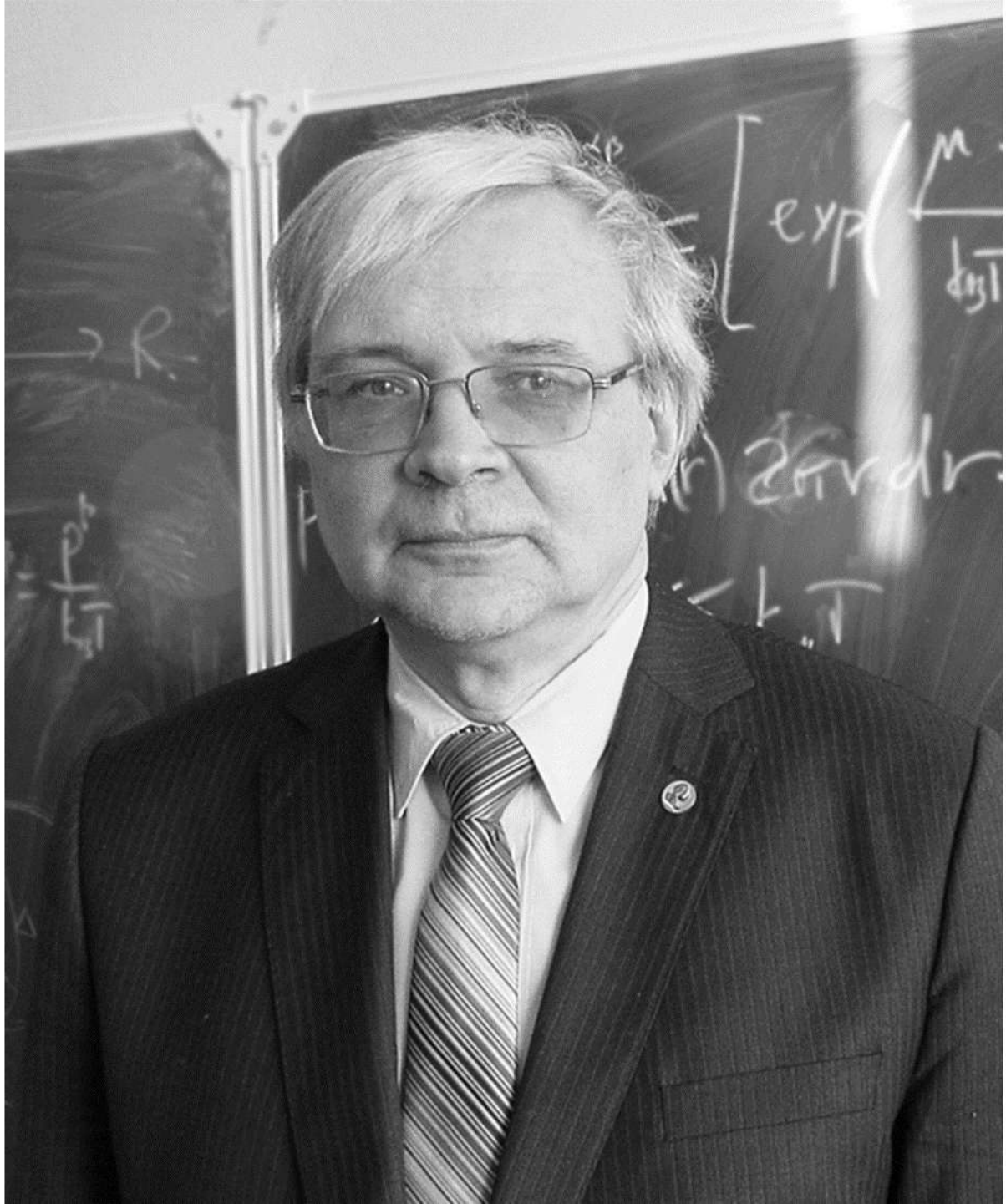
Department of Statistical Physics
Faculty of Physics
Saint Petersburg State University

To the memory of

Dr.Sc., Corr. Member of RAS

Alexander Kimovich Shchekin

28.07.1957 – 12.07.2023



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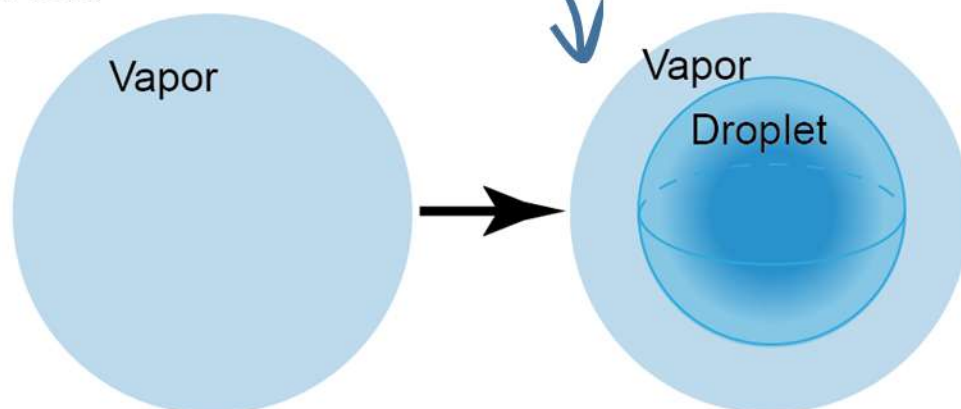

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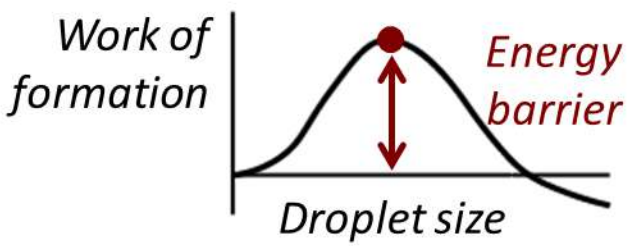
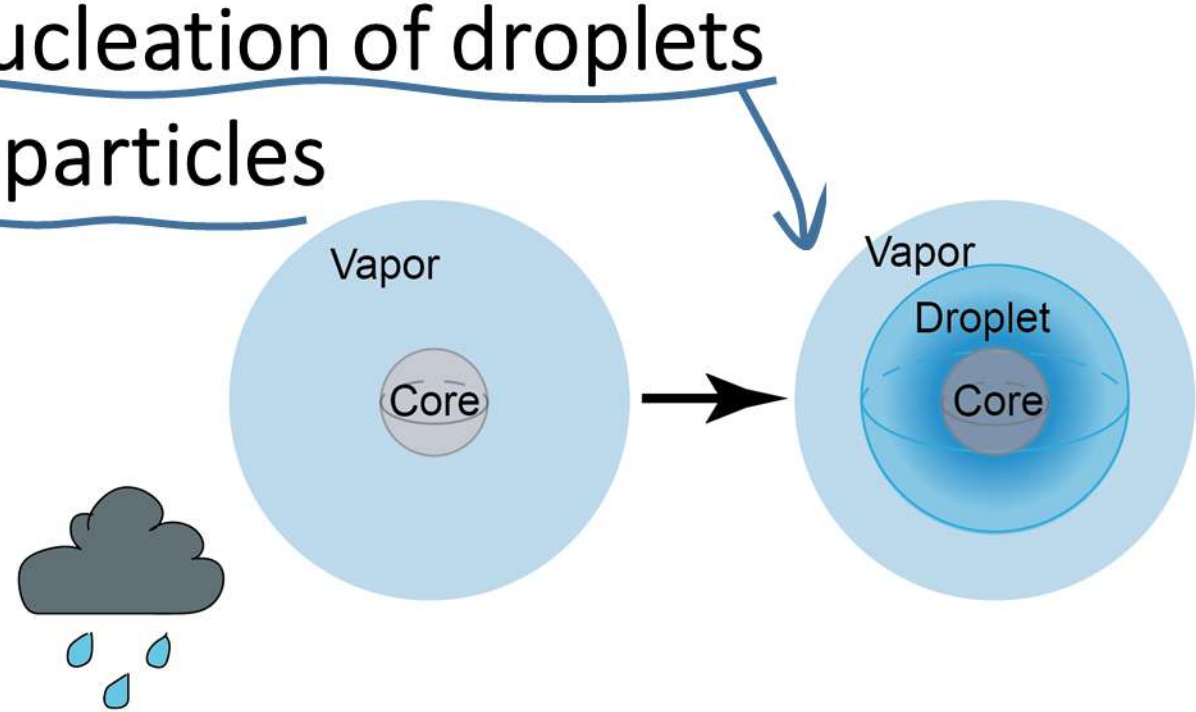
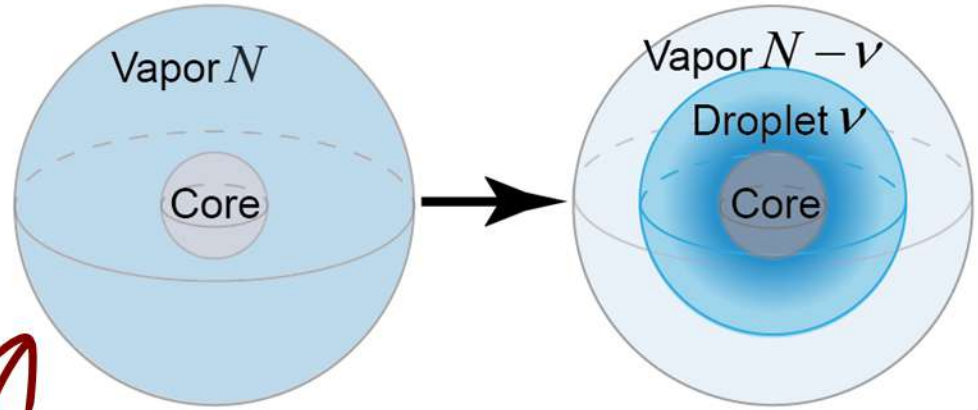


That's what happens in nature!

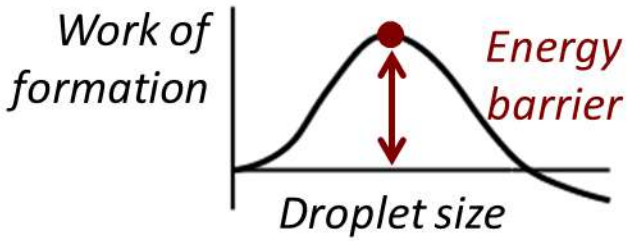




***N* = finite**
A closed system
(Canonical Ensemble)

- in computer simulation
- in reality (in a small pore)

Confinement effects in heterogeneous nucleation of droplets on solid particles



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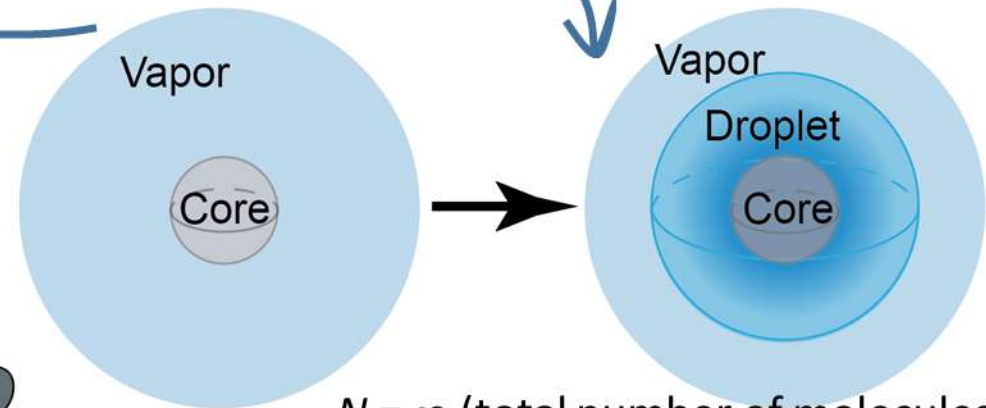


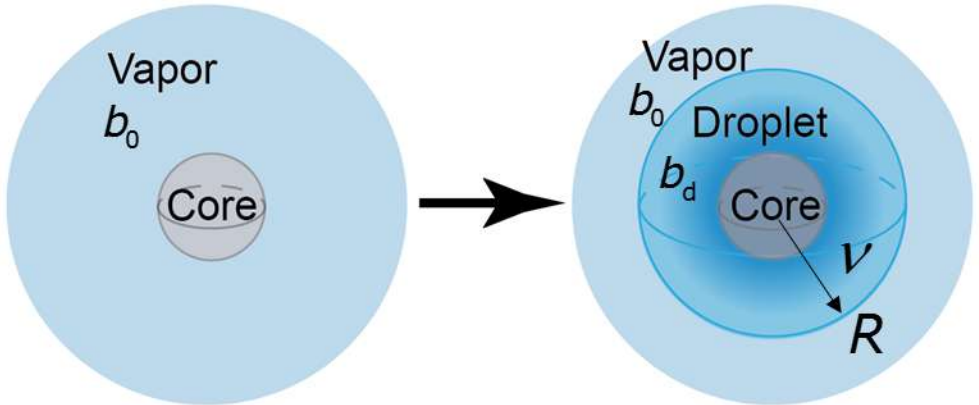
$N = \infty$ (total number of molecules)
An open system
(Grand Canonical Ensemble)

Plan

1. Thermodynamic “macro” description
2. Classical density functional theory “micro” calculations

Thermodynamic “macro” description

Open systems (Grand Canonical Ensemble)



$$b \equiv \frac{\mu - \mu_\infty}{k_B T}$$

b_0 – initial vapor chemical potential

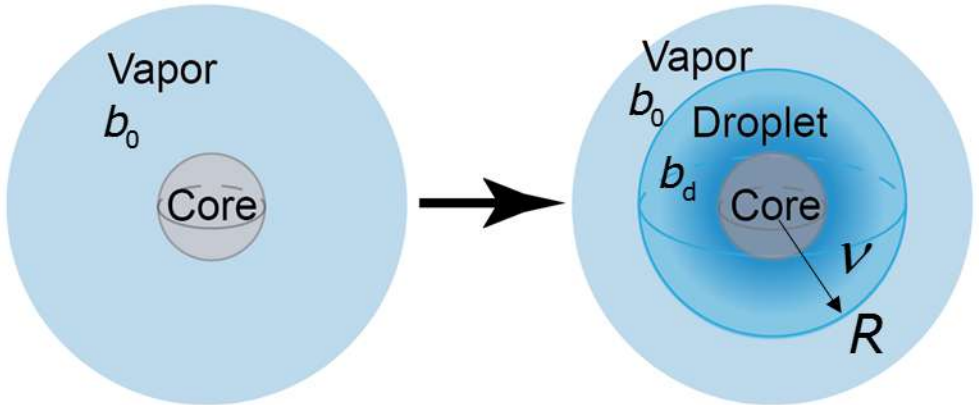
b_d – chemical potential in the droplet

$b_d(v) = b_0$ - at equilibrium

$$b_d \approx \frac{2\gamma}{k_B T n^\alpha R} - \frac{K \exp\left(-\frac{R - R_{core}}{\lambda}\right)}{k_B T n^\alpha} \frac{R_{core}^2}{R^2}$$

Surface tension Disjoining pressure

Open systems (Grand Canonical Ensemble)



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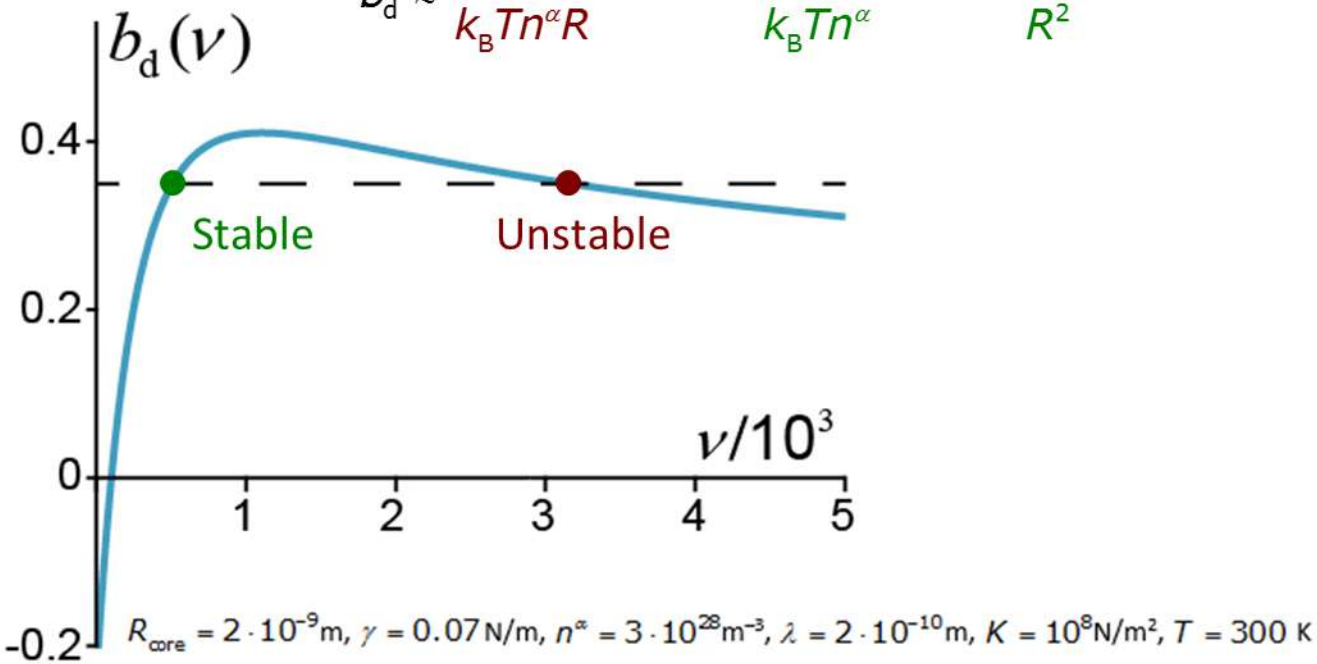

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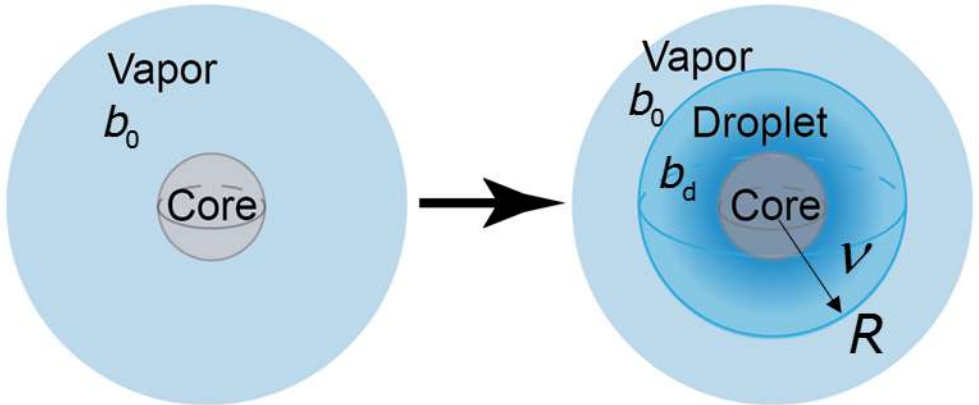

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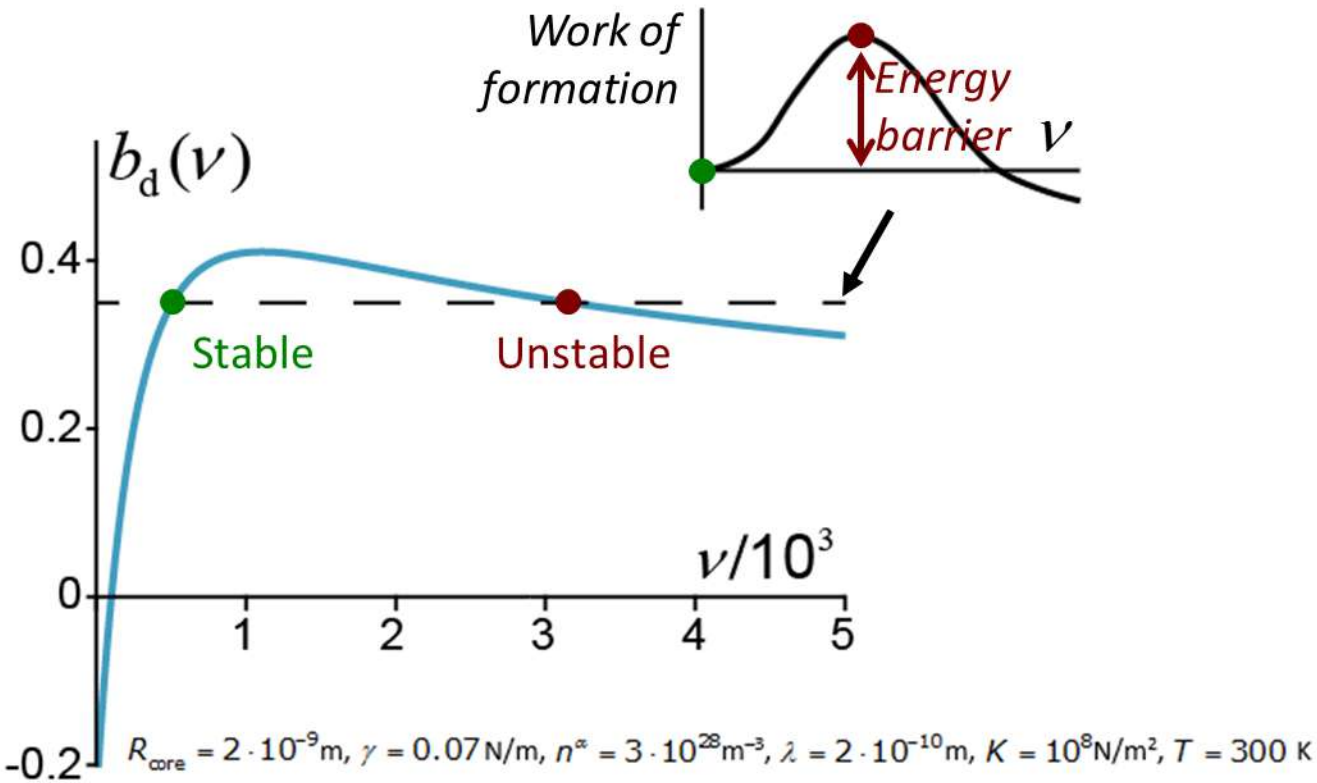

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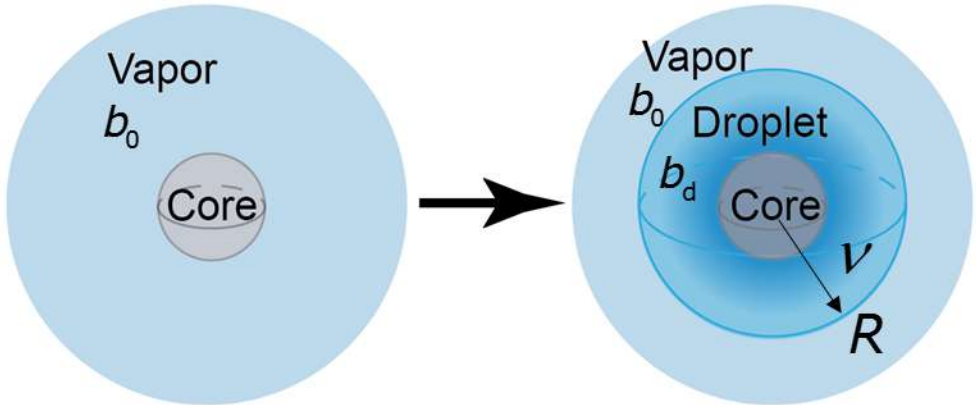

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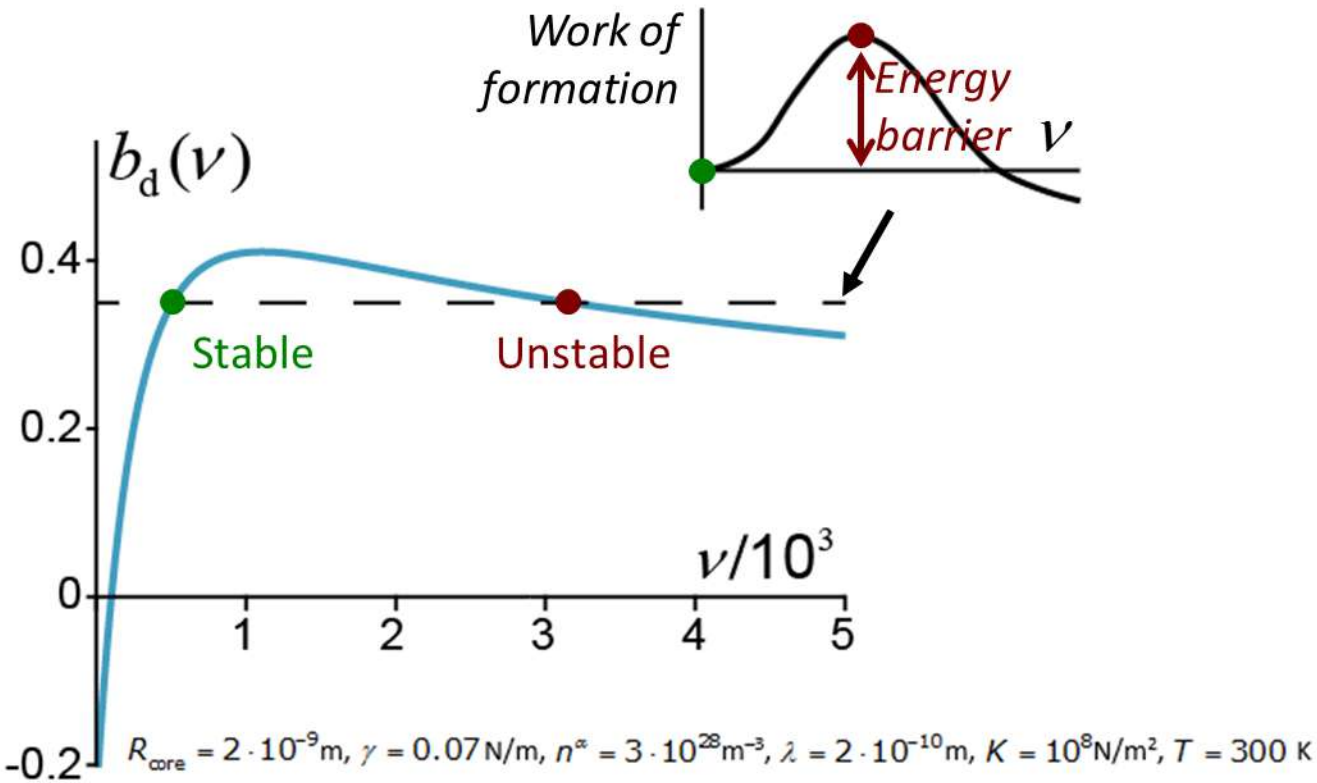
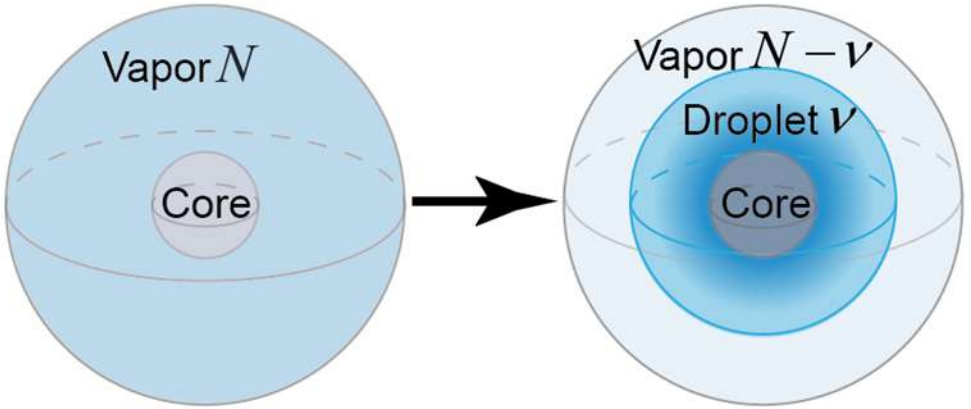


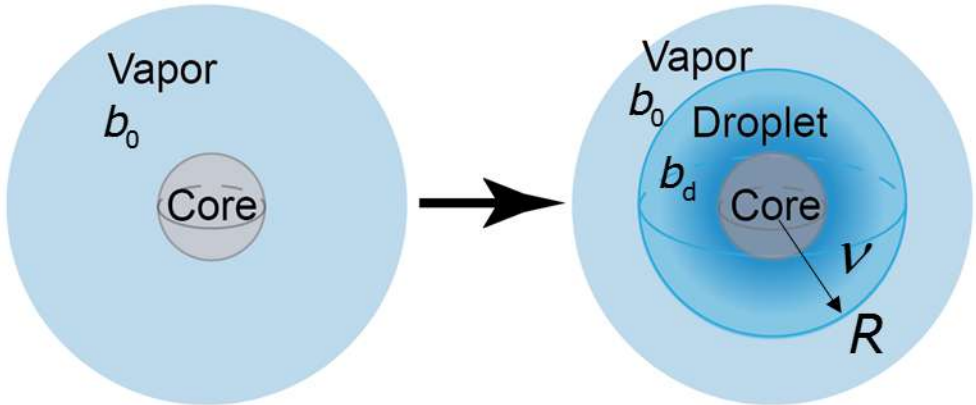
Closed systems (Canonical Ensemble)



$b_d = b_0 + \ln(1 - \nu / N)$

Ideal gas approximation for the vapor phase

Open systems (Grand Canonical Ensemble)



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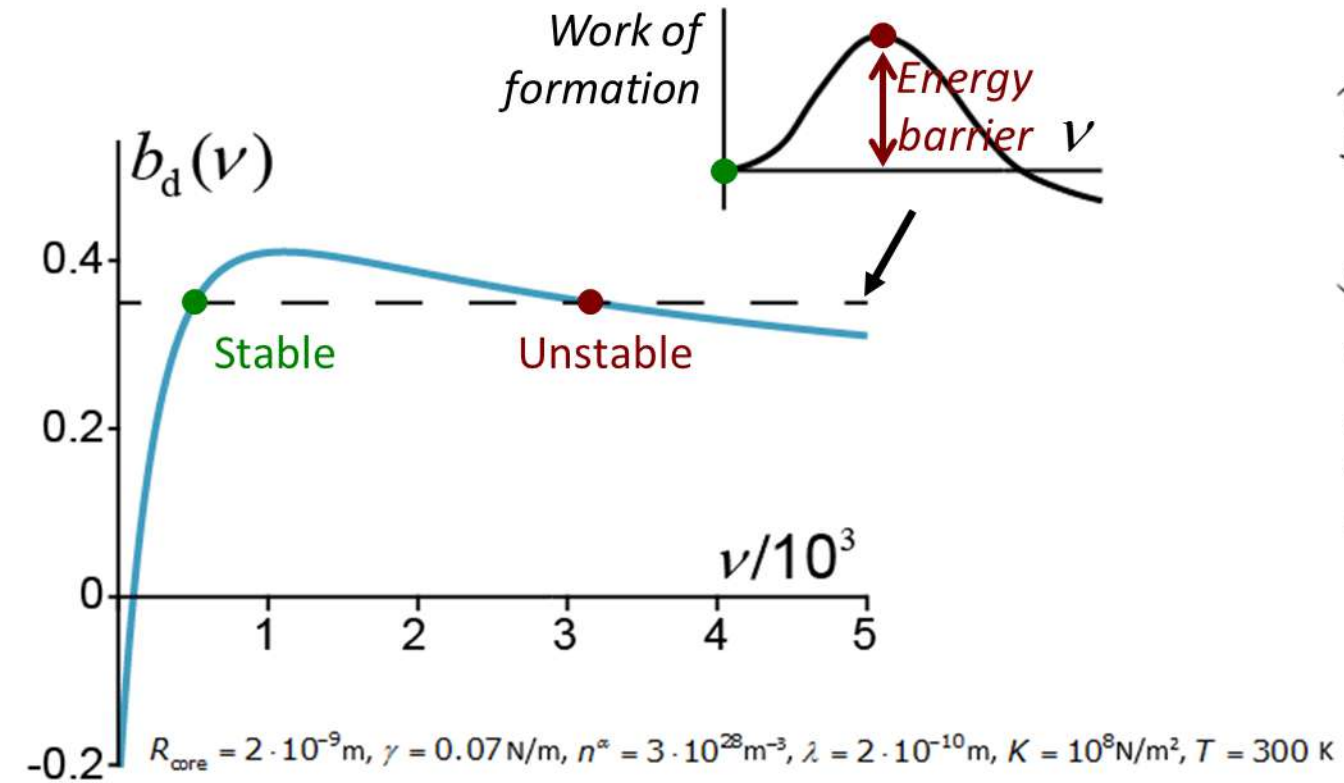
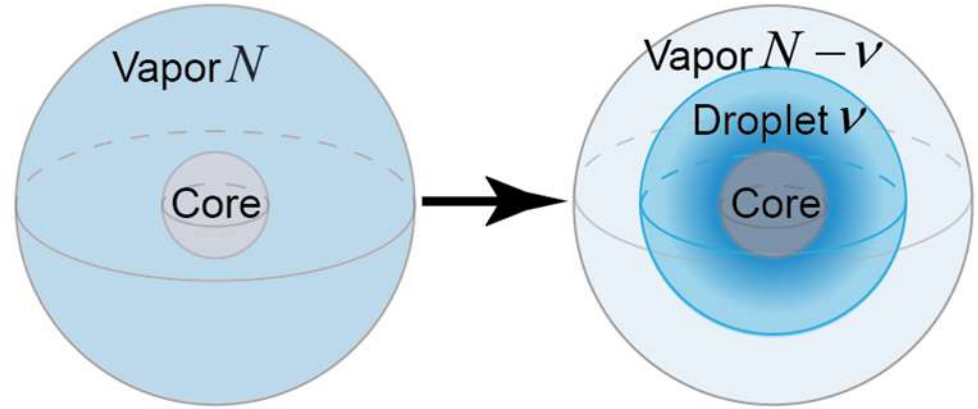


$R_{core} = 2 \cdot 10^{-9}$m, $\gamma = 0.07$ N/m, $n^{\infty} = 3 \cdot 10^{28}$m^{-3}, $\lambda = 2 \cdot 10^{-10}$m, $K = 10^8$N/m^2, $T = 300$ K

Closed systems (Canonical Ensemble)



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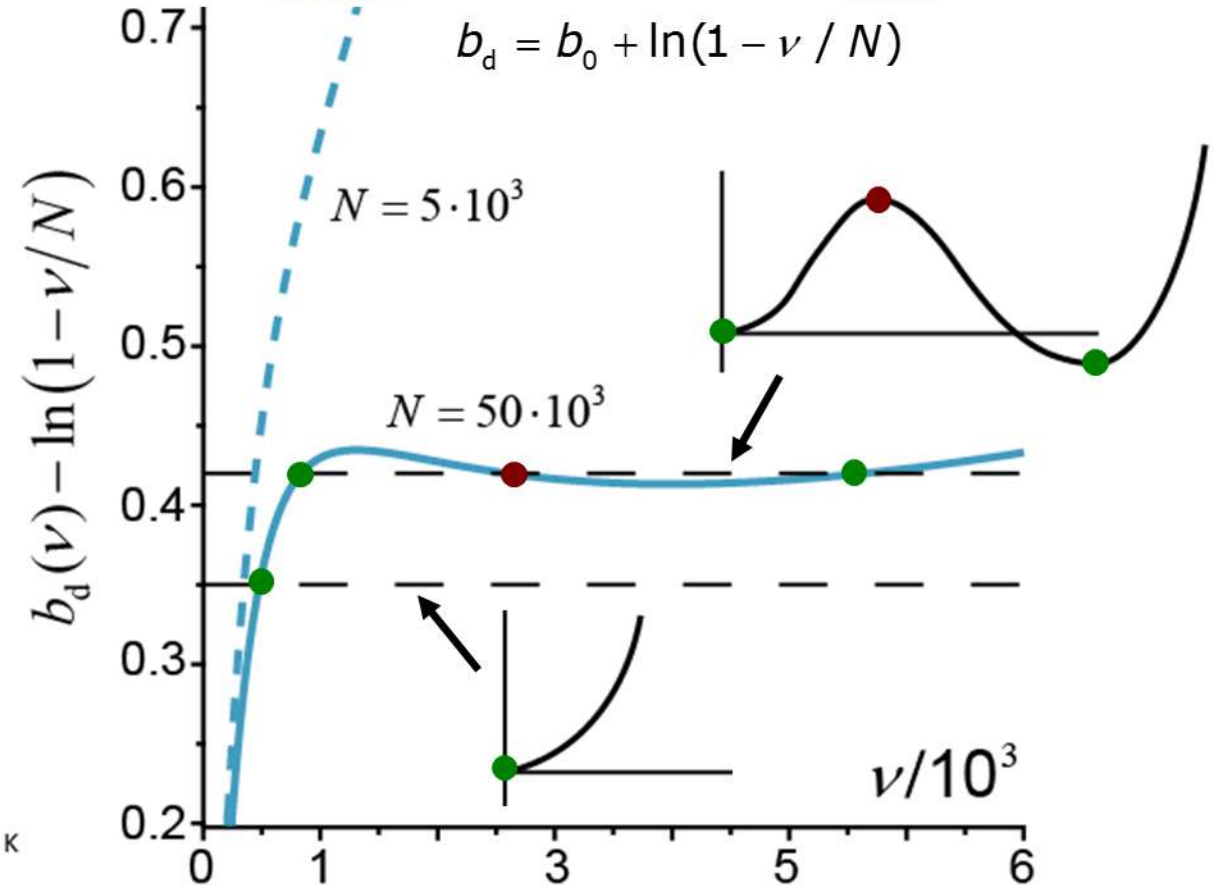

Classical density functional theory (DFT)

Density functional theory (DFT)

$\frac{\delta F[\rho]}{\delta \rho} = 0 \Rightarrow$ an equation for the density profile $\rho(\vec{r})$ at equilibrium $\begin{cases} \text{stable} - \text{minimum} \\ \text{unstable} - \text{saddle point} \end{cases}$

$F = ?$ various models...

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$F = ?$ various models...

1. Square-gradient DFT *R. Evans (1979)*

$$F[\rho(\vec{r})] = F_{\text{ideal}} + \int d\vec{r} \left(-a\rho(\vec{r})^2 + \frac{C}{2}(\nabla\rho(\vec{r}))^2 \right) + k_B T \int d\vec{r}\, \rho(\vec{r})\, \frac{4\eta(\vec{r}) - 3\eta(\vec{r})^2}{(1-\eta(\vec{r}))^2} + \int d\vec{r}\, v_{\text{ext}}(\vec{r})\rho(\vec{r}), \qquad \eta \equiv \frac{\pi d^3}{6}\rho$$

Long-range attraction

Hard-sphere repulsion (Carnahan–Starling)

+ assumption of spherical symmetry

2. DFT + Fundamental Measure Theory *R. Roth et al. (2002)*

$$F[\rho(\vec{r})] = F_{\text{ideal}} + \frac{1}{2}\iint d\vec{r}\, d\vec{r}'\, \rho(\vec{r})\, u(|\vec{r} - \vec{r}'|)\, \rho(\vec{r}') + k_B T \int d\vec{r}\, \Phi(\{n_\alpha(\vec{r})\}) + \int d\vec{r}\, v_{\text{ext}}(\vec{r})\rho(\vec{r})$$

Long-range attraction

Hard-sphere repulsion (Fundamental Measure Theory)

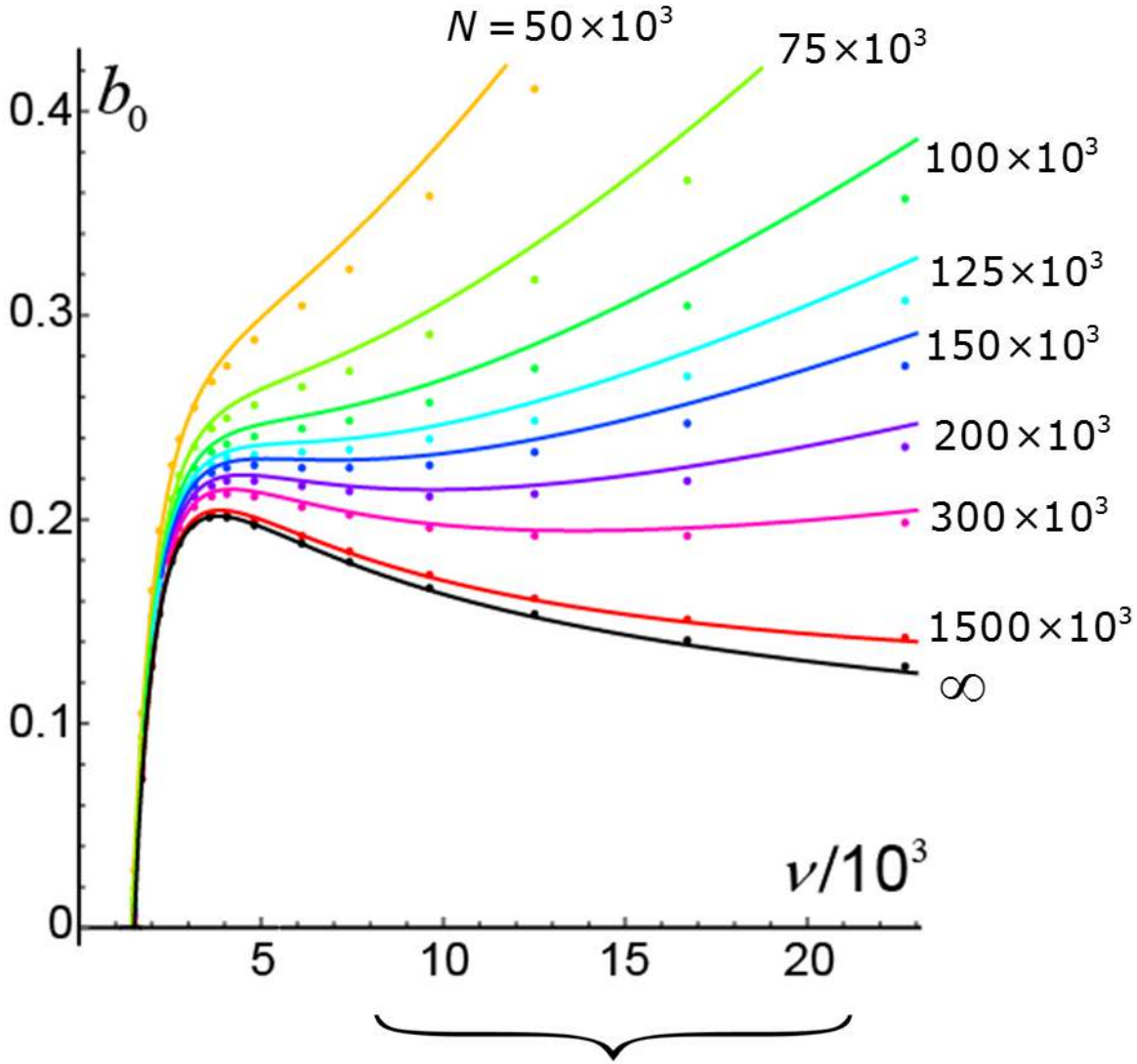
$$n_\alpha(\vec{r}) \equiv \int d\vec{r}'\, \rho(\vec{r}')\, \omega_\alpha(\vec{r} - \vec{r}')$$

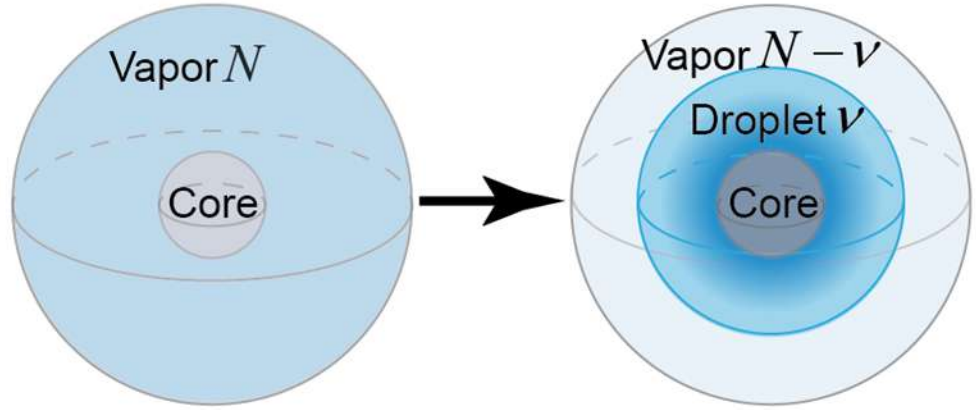
A library for DFT calculations:
J. Lutsko, classicalDFT.
github.com/jimlutsko/classicalDFT.

DFT results for closed systems

Results

1. Square-gradient DFT, large *N*





$R_{core} = 4d_{molecule}$

Dots – DFT

Curves – thermodynamics (fitting)

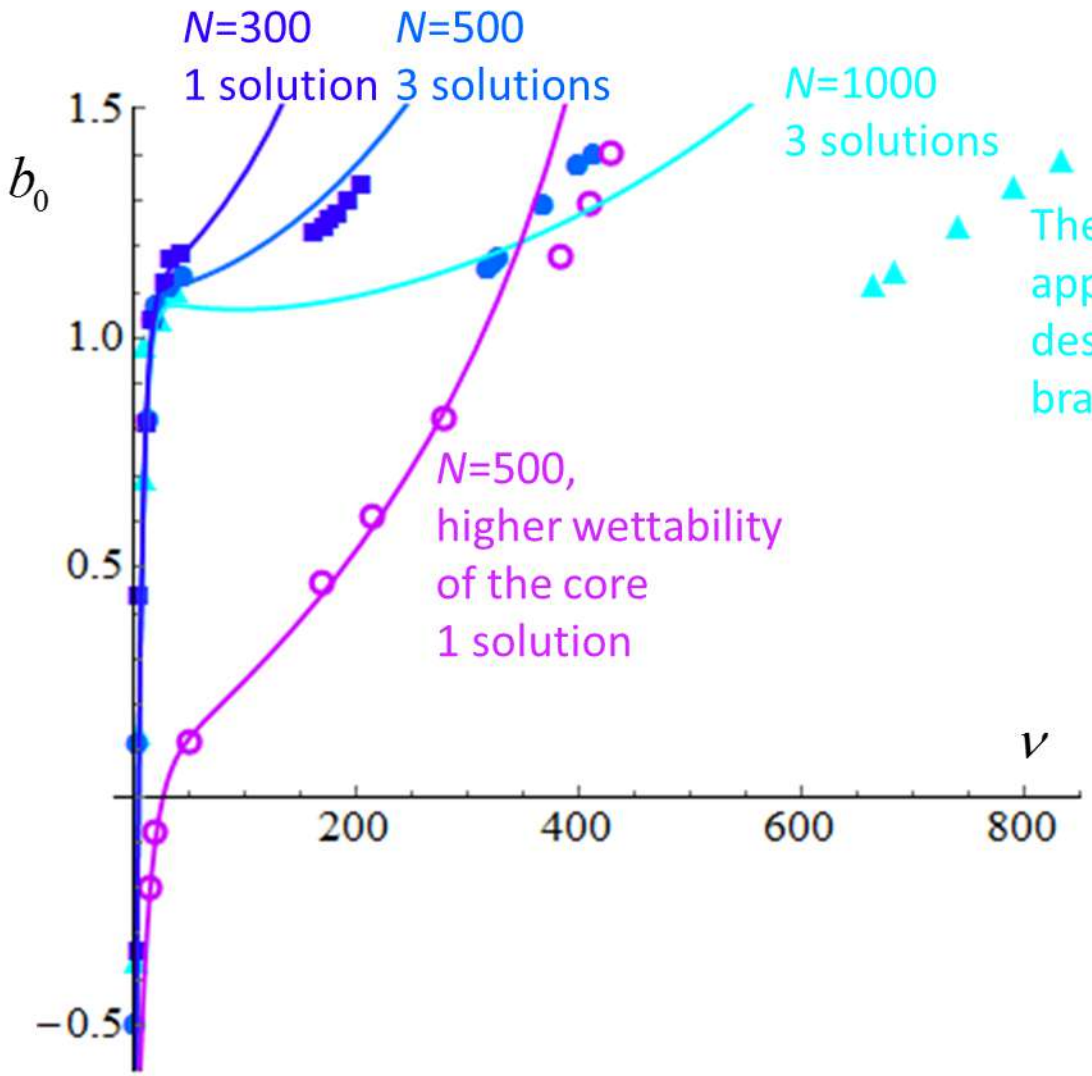
The dependence of the initial vapor chemical potential b_0 on the number ν of droplet's molecules with different total numbers N of argon-like fluid molecules in a closed system.

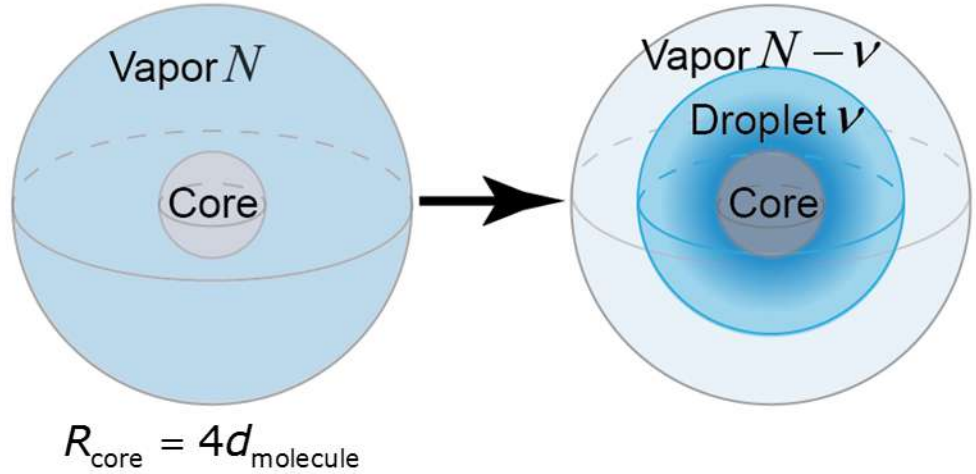
$T = 90\,\mathrm{K},\ a = 3.58\cdot10^{-49}\ \mathrm{J\cdot m^3},\ C = 0.551d^5k_BT,\ d = 3.14\cdot10^{-10}\,\mathrm{m}$

ν is not close to N ⇒ The ideal-gas approximation works

Results

2. Fundamental Measure DFT, small *N*



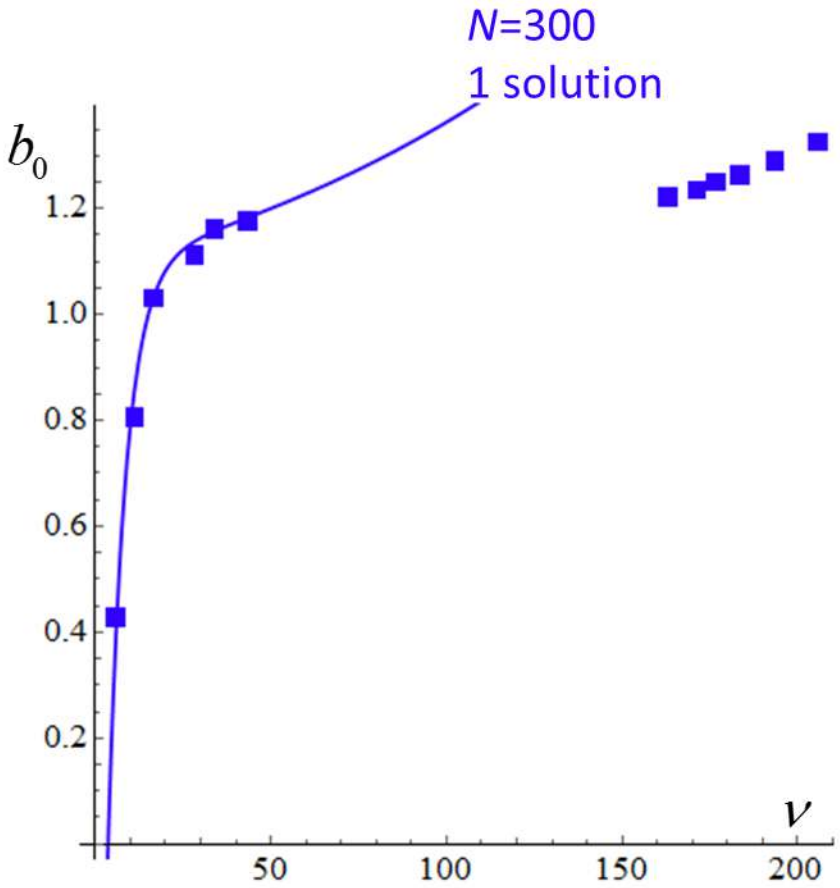


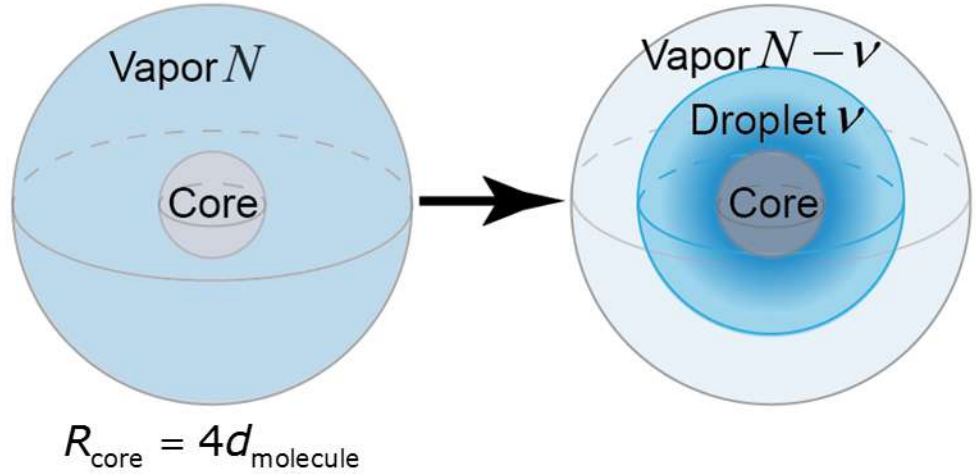
Dots – DFT
Curves – thermodynamics (fitting)

The dependence of the initial vapor chemical potential b_0 on the number ν of droplet's molecules with different total numbers N of argon-like fluid molecules in a closed system.
Only stable solutions are depicted.

Results

2. Fundamental Measure DFT, small *N*





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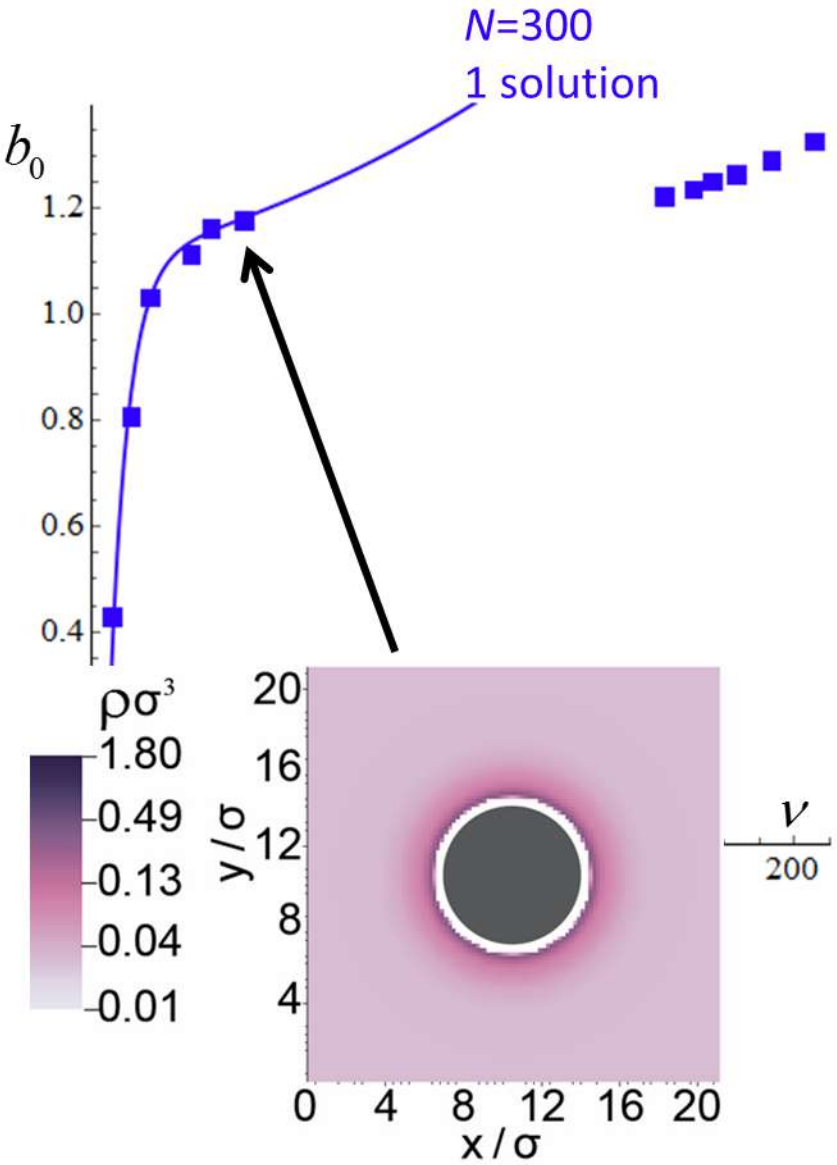

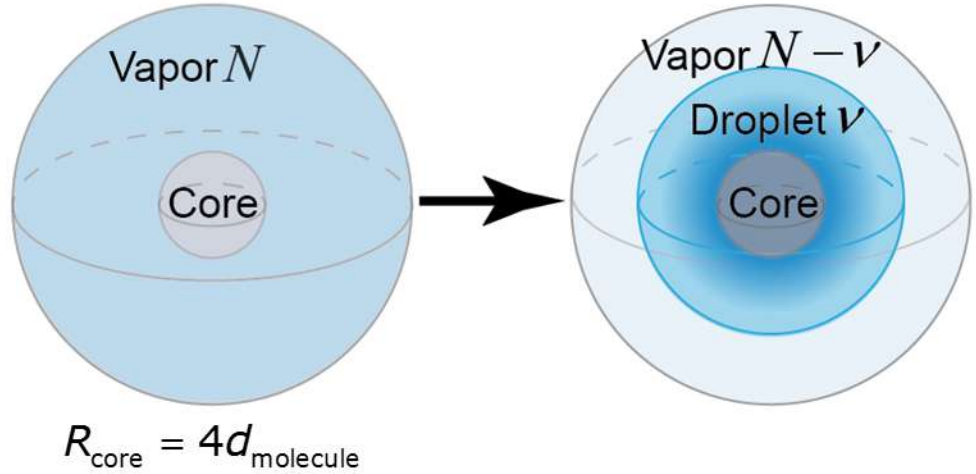

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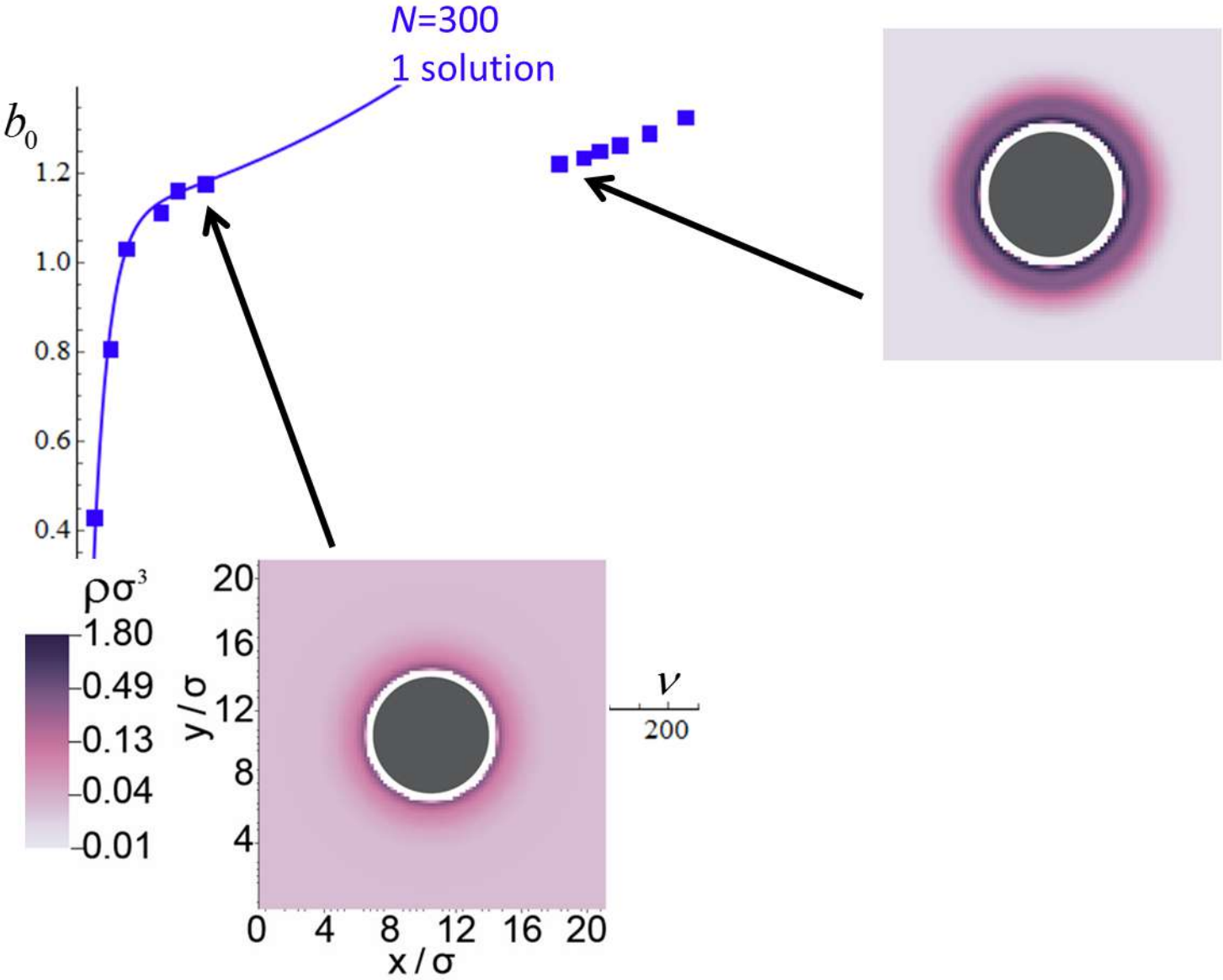

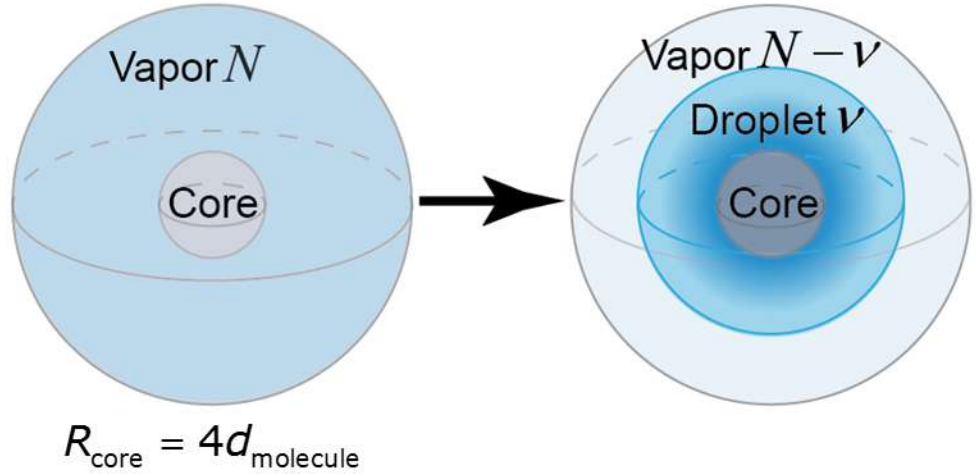

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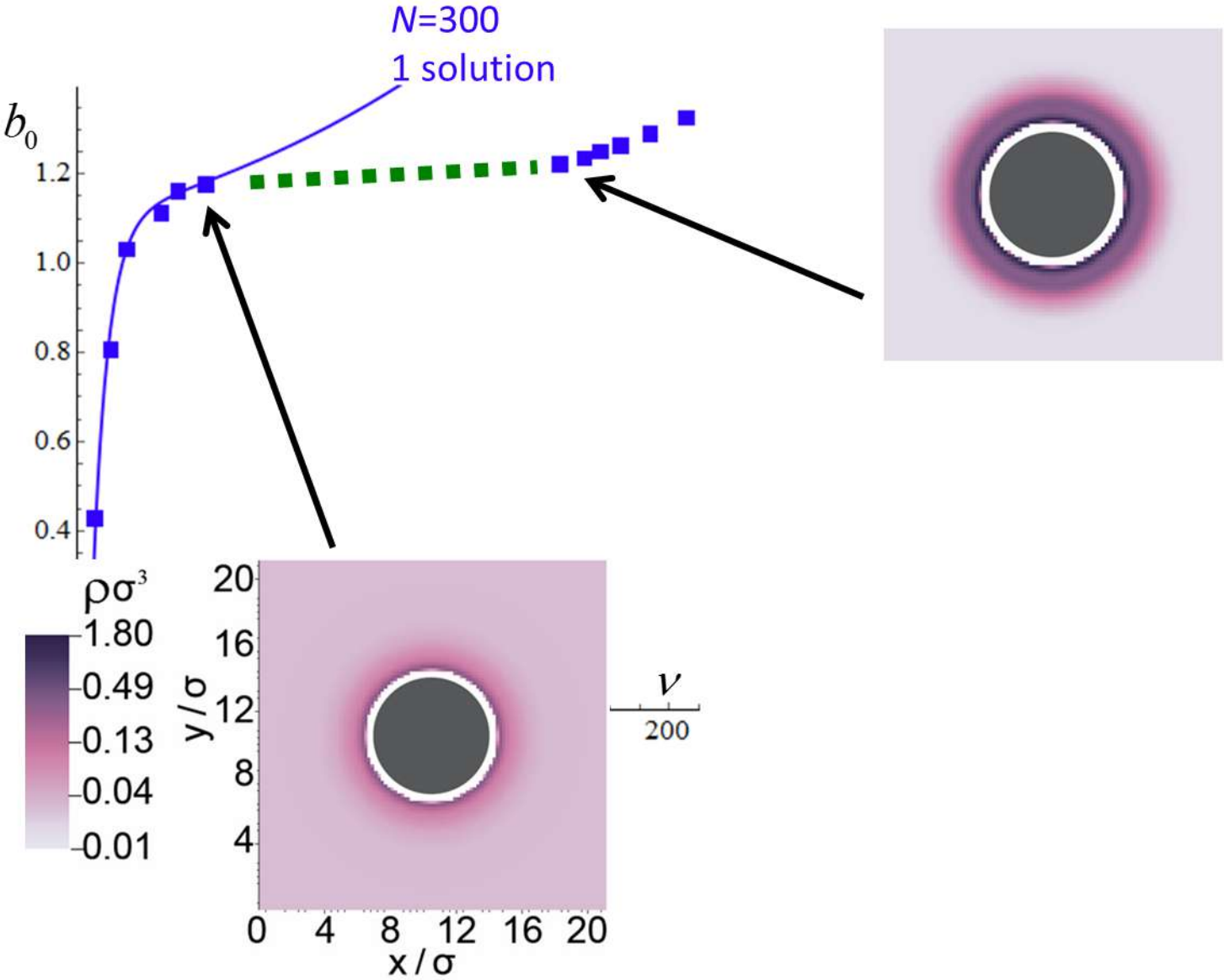

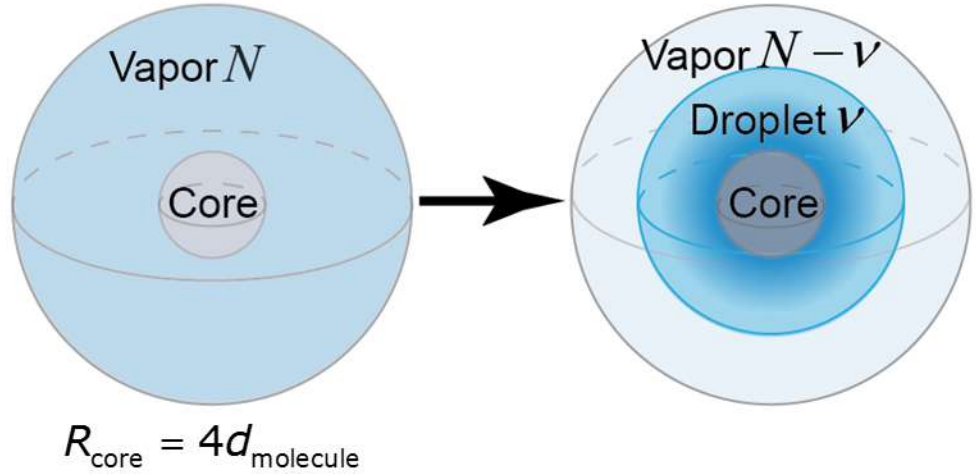

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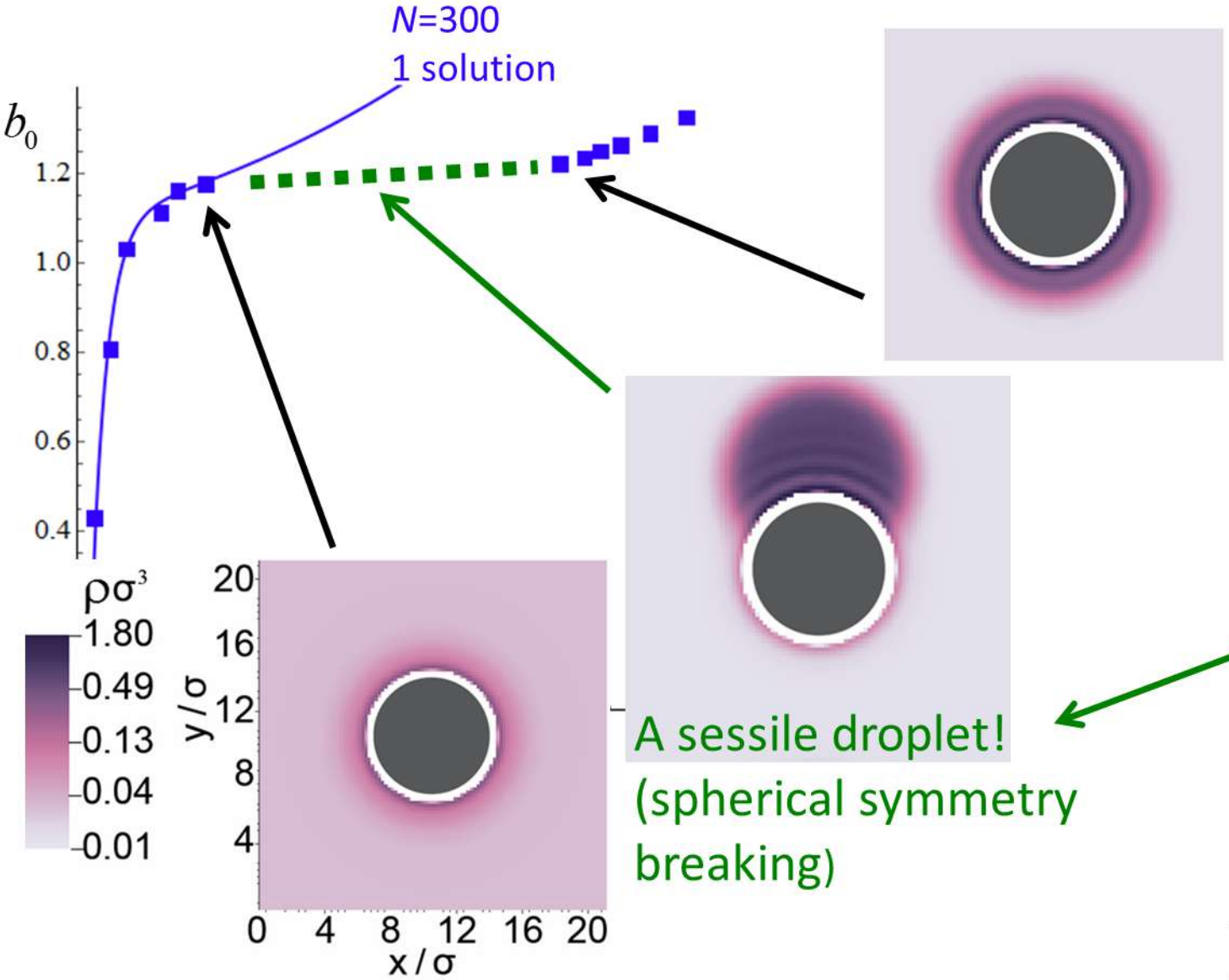
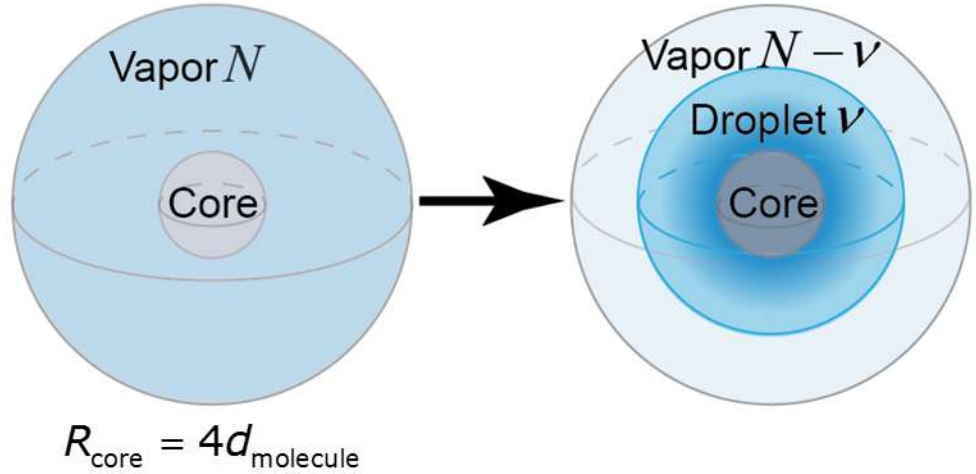
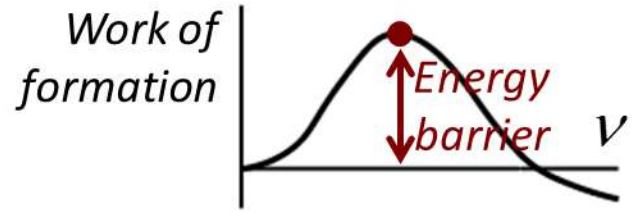


A sessile droplet!
(spherical symmetry breaking)



It's interesting not only for closed systems:

Stable in CE ↔ unstable in GCE



⇒ in some region of parameters, the transition over the sessile droplet state is more energy-efficient than the transition over the spherical droplet state

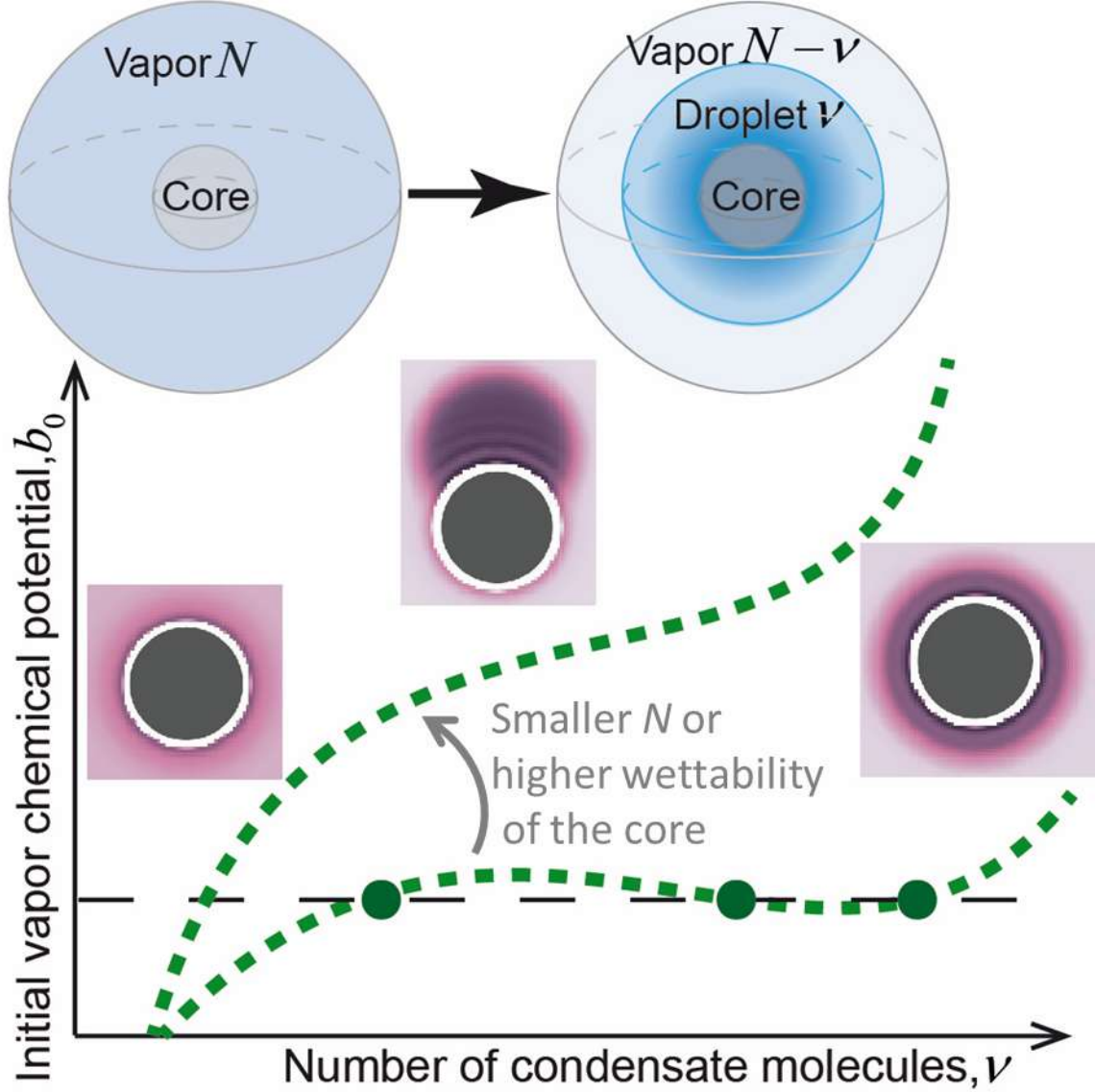
Conclusions

1. Confinement → 1 solution OR 3 solutions

2. The ideal-gas approximation for the vapor phase describes only the left branch of the chemical potential (small droplets)

3. The sessile droplet formation (spherical symmetry breaking) in the case of low molecule number *N* and high initial supersaturation

4. It corresponds to the unstable solution in GCE (an easy way to find a saddle point – to find a minimum in the corresponding CE)



Thanks for your attention!

References

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