FACET

Functional Materials and Materials Chemistry

Physical Validation of Properties of Small Grand Canonical Systems

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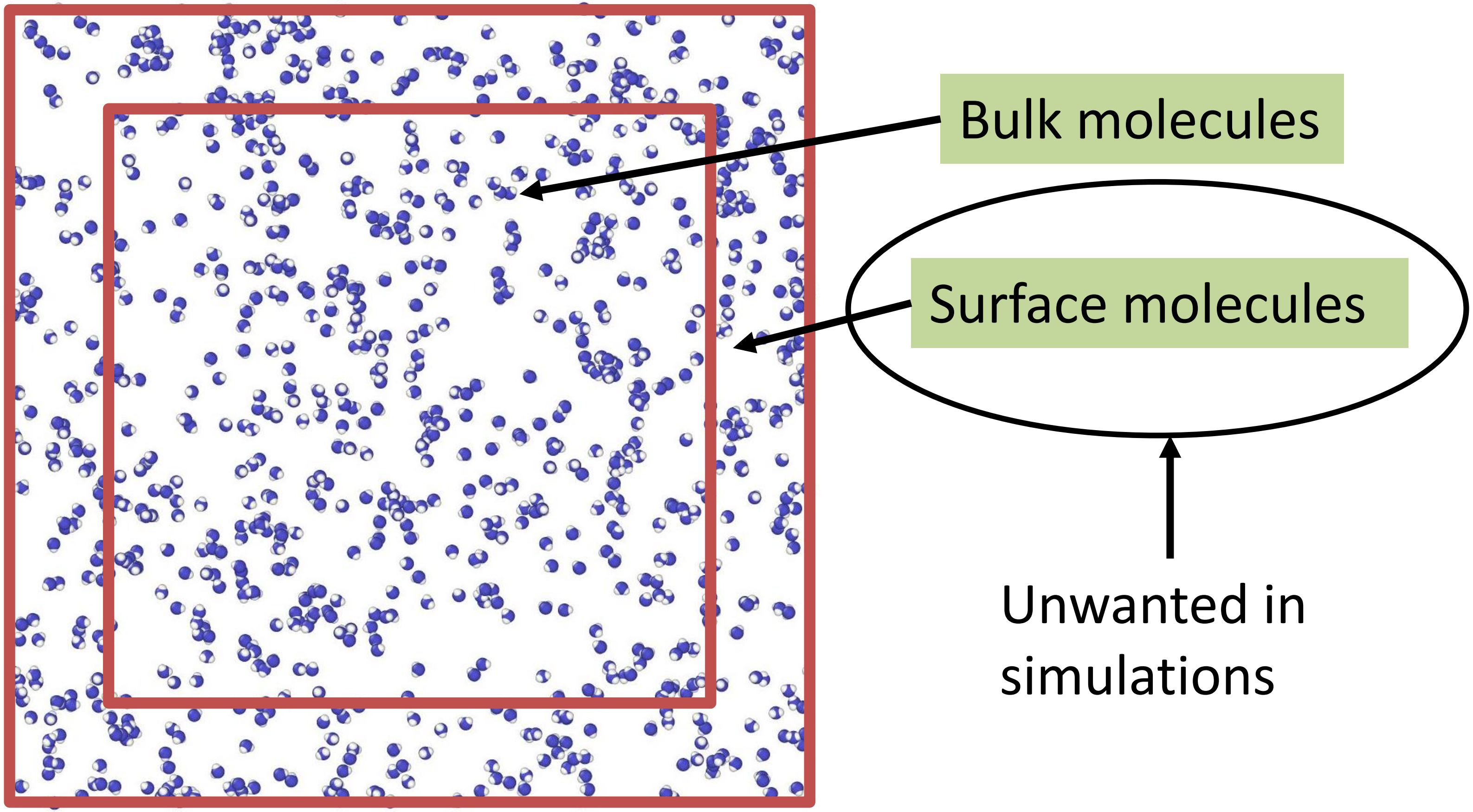
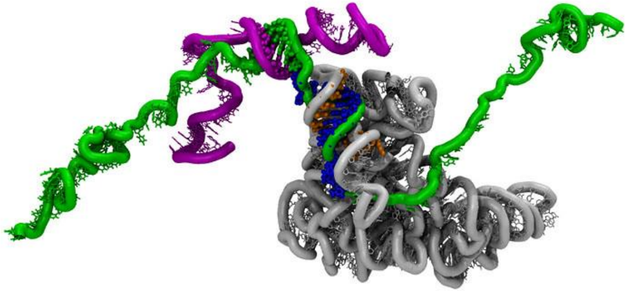
$$\frac{\Omega}{V}$$

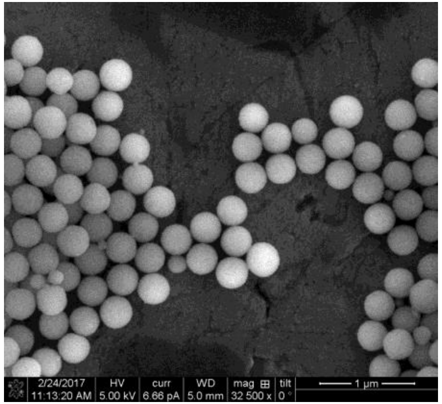
Small in macroscopic systems

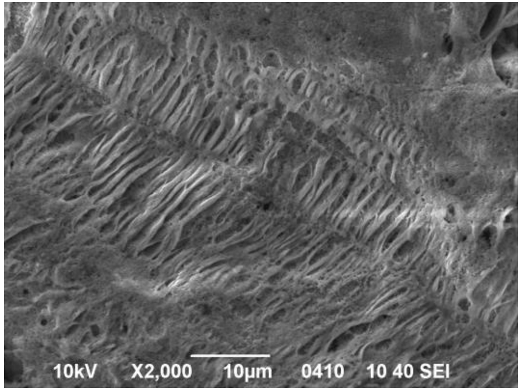
Large in small systems

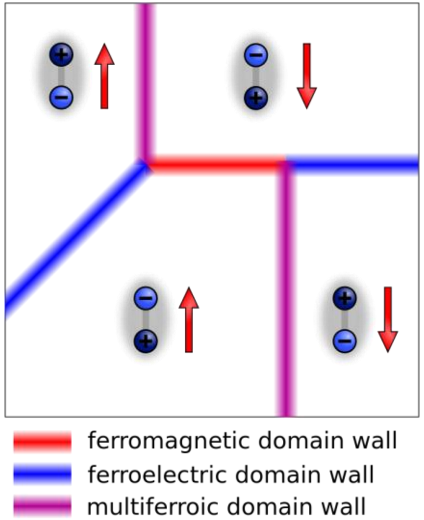

Bulk molecules
Surface molecules
Unwanted in simulations

Nanosystems









Nanothermodynamics

Isobaric-isothermal

- Macroscopic

$$G = \mu N$$

- Small system

$$G = \hat{\mu} N$$

Grand canonical

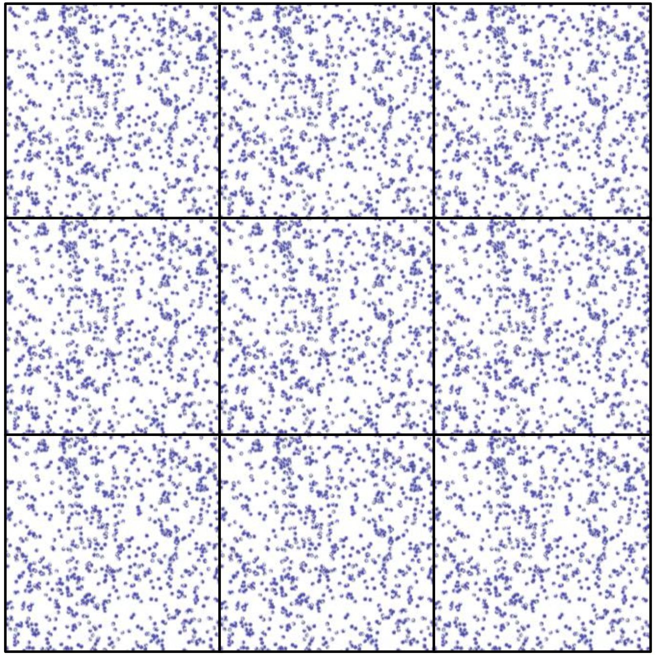
- Macroscopic

$$-pV$$

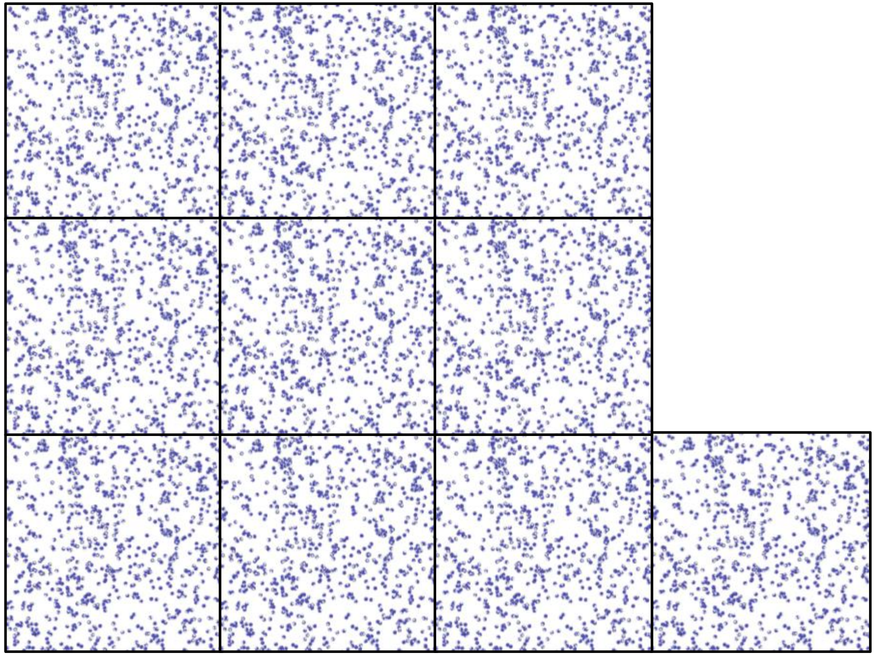
- Small system

$$-\hat{p}V$$

Differential



Integral



Small size contribution = excess property

Differential

$$p = p^{\infty} + p^{\mathrm{small}}$$

Integral

$$\hat{p} = p^{\infty} + \hat{p}^{\mathrm{small}}$$

$$p = \hat{p}$$

in the macroscopic limit

Nanothermodynamics

Isobaric-isothermal

$$S = -\left(\frac{\partial \hat{\mu} N}{\partial T}\right)_{p,N}$$

$$V = -\left(\frac{\partial \hat{\mu} N}{\partial T}\right)_{T,N}$$

$$\mu = -\left(\frac{\partial \hat{\mu} N}{\partial T}\right)_{p,T}$$

Grand canonical

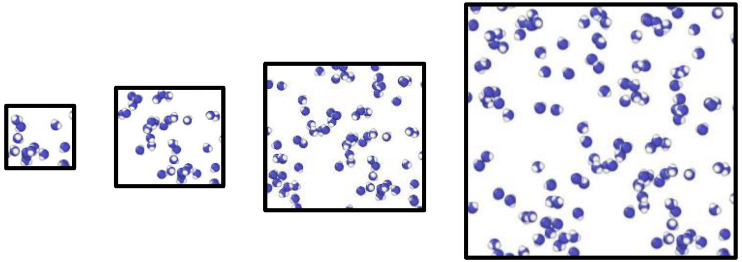
$$S = \left(\frac{\partial \hat{p} V}{\partial T}\right)_{\mu,V}$$

$$p = \left(\frac{\partial \hat{p} V}{\partial V}\right)_{\mu,T}$$

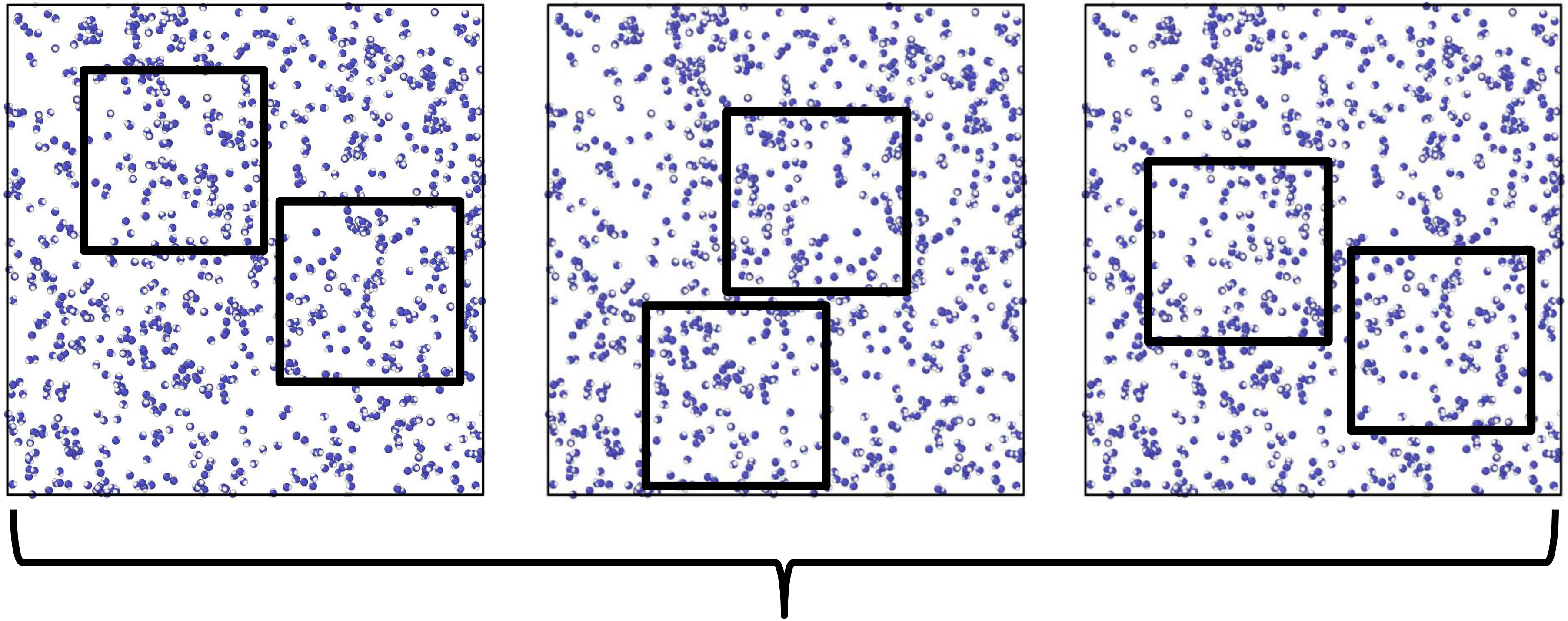
$$N = \left(\frac{\partial \hat{p} V}{\partial \mu}\right)_{V,T}$$

Challenges

- Many simulations → time consuming



- Calculation of free energies
  - Macroscopic methods does not work for small systems



Grand canonical particle fluctuations

Connection to partition function

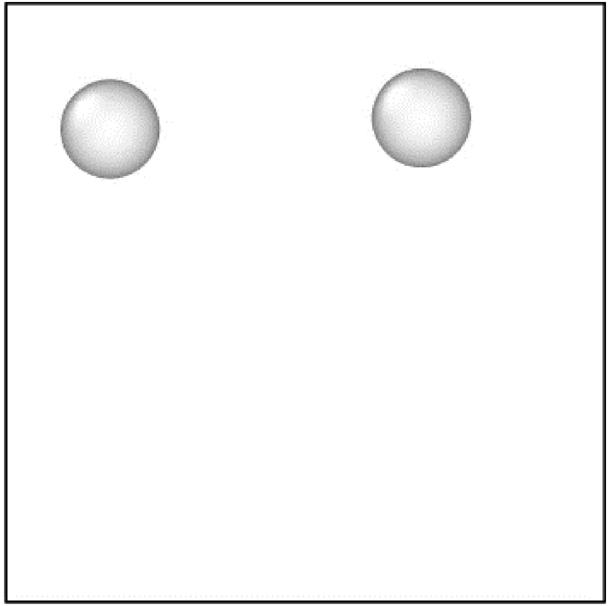
$$\hat{p}V = k_\mathrm{B}T \ln \Xi(\mu, V, T)$$

$$S = \left(\frac{\partial \hat{p}V}{\partial T}\right)_{\mu,V}$$

$$p = \left(\frac{\partial \hat{p}V}{\partial V}\right)_{\mu,T}$$

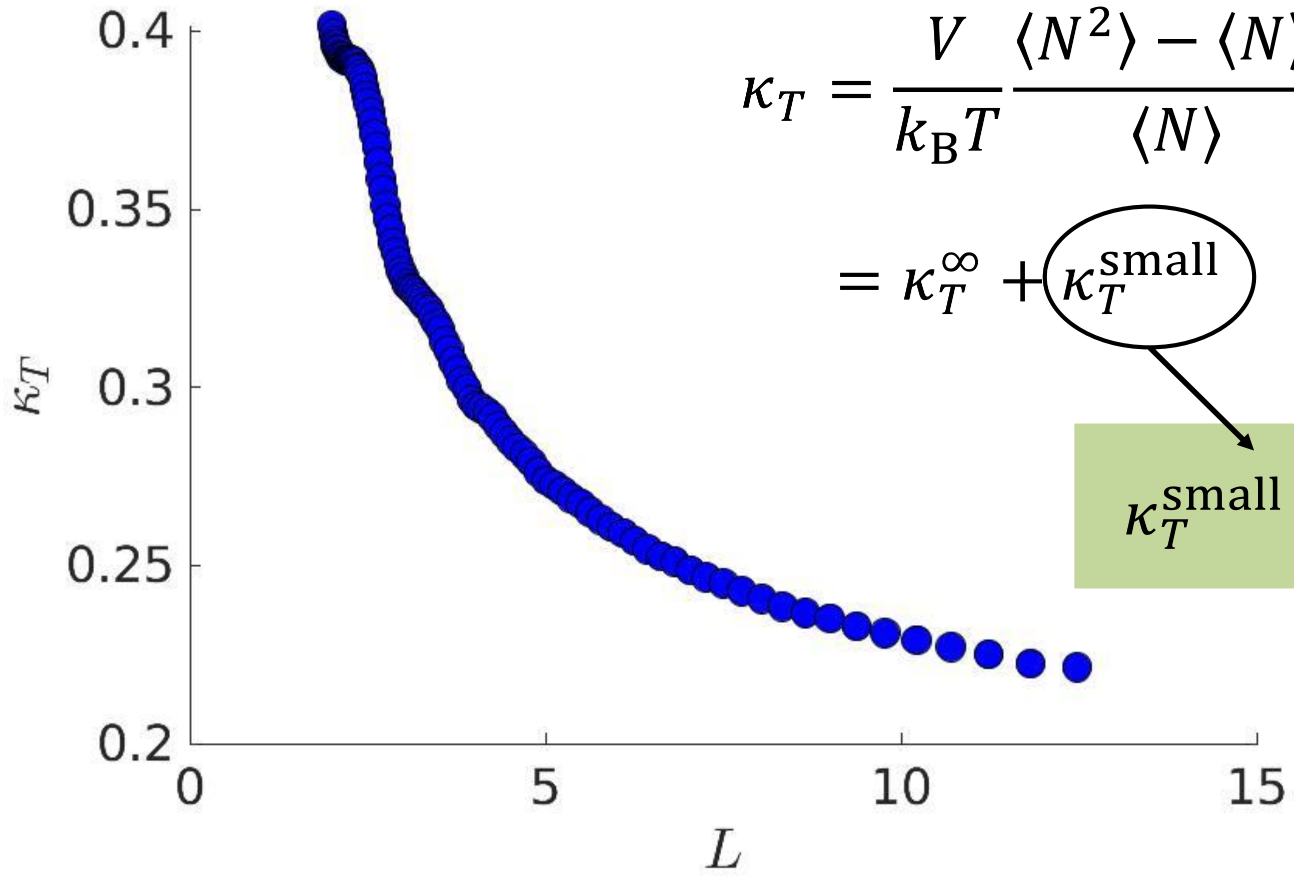
$$N = \left(\frac{\partial \hat{p}V}{\partial \mu}\right)_{V,T}$$

$$(k_\mathrm{B}T)^2 \left(\frac{\partial^2 \ln \Xi}{\partial \mu^2}\right)_{T,V} = \langle N^2 \rangle - \langle N \rangle^2$$



$$\langle N^2 \rangle - \langle N \rangle^2$$

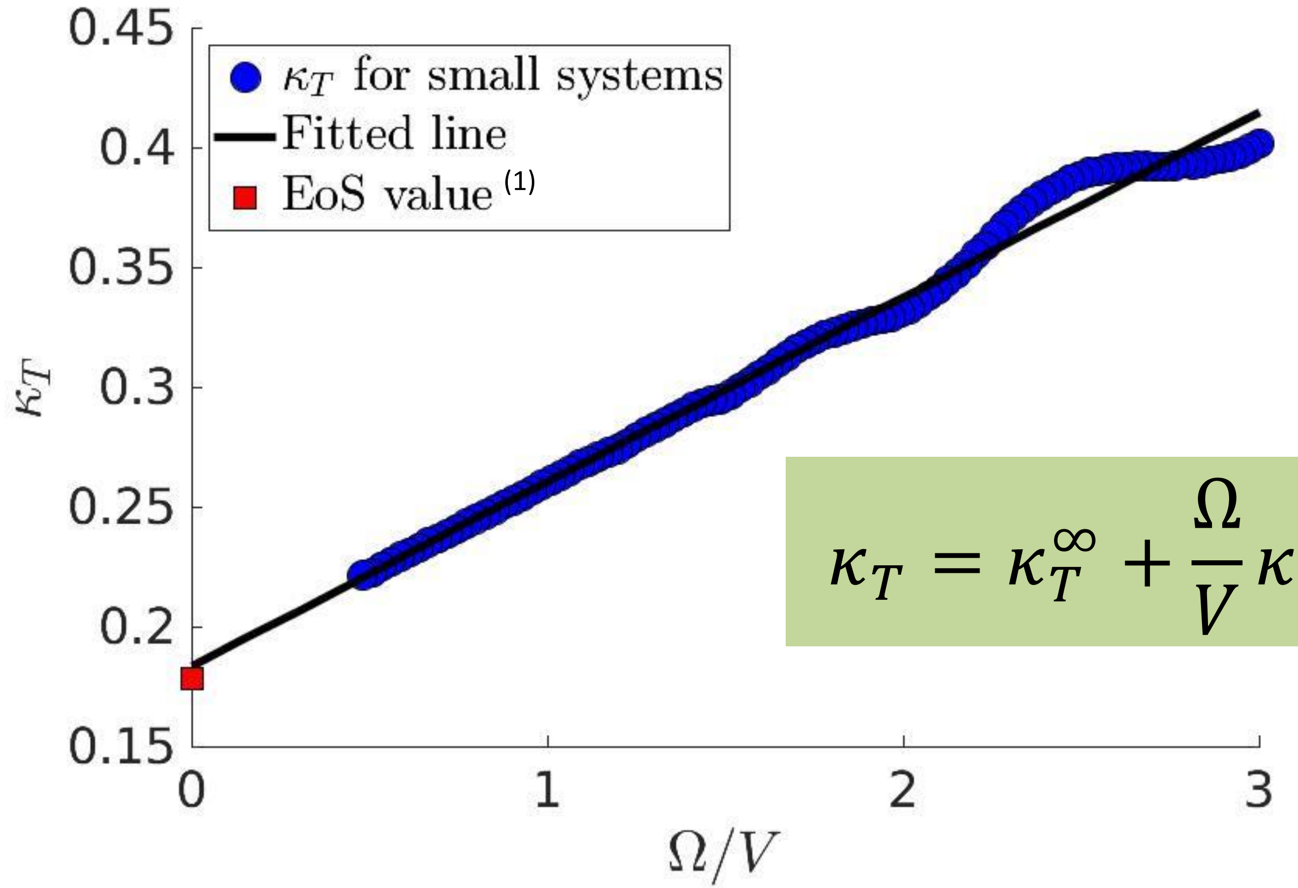
$$\kappa_T, C_p, V_i, H_i, G_{ij} \ldots$$



$$\kappa_T = \frac{V}{k_\mathrm{B}T}\frac{\langle N^2\rangle - \langle N\rangle^2}{\langle N\rangle}$$

$$= \kappa_T^\infty + \kappa_T^\mathrm{small}$$

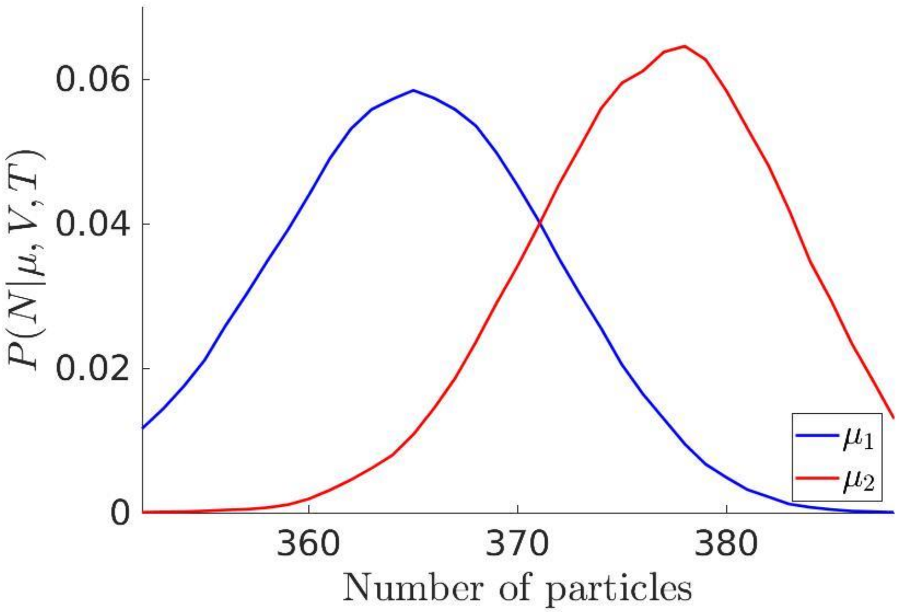
$$\kappa_T^\mathrm{small} = \frac{\Omega}{V}\kappa_T^\mathrm{surf}$$



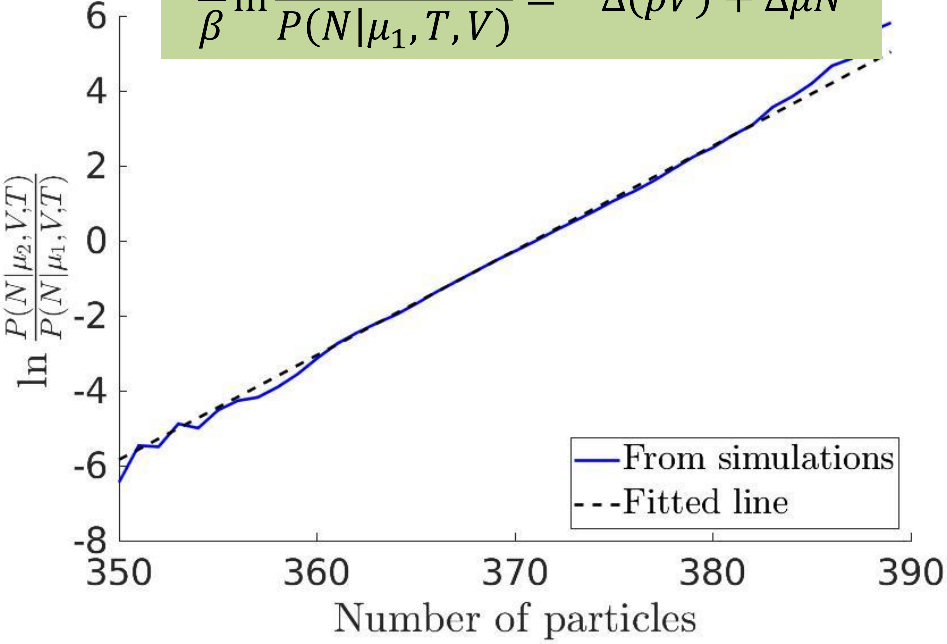
$$\kappa_T = \kappa_T^{\infty} + \frac{\Omega}{V}\kappa_T^{\text{surf}}$$

(1) Span, R.; Beckmüller, R.; Eckermann, T.; Herrig, S.; Hielscher, S.; Jäger, A.; Mickoleit, E.; Neumann, T.; Pohl S. M.; Semrau, B.; Thol, M. (2019): *TREND. Thermodynamic Reference and Engineering Data 4.0*. Lehrstuhl für Thermodynamik, Ruhr-Universität Bochum.

Ensemble check[2] = Overlapping distribution method[3]

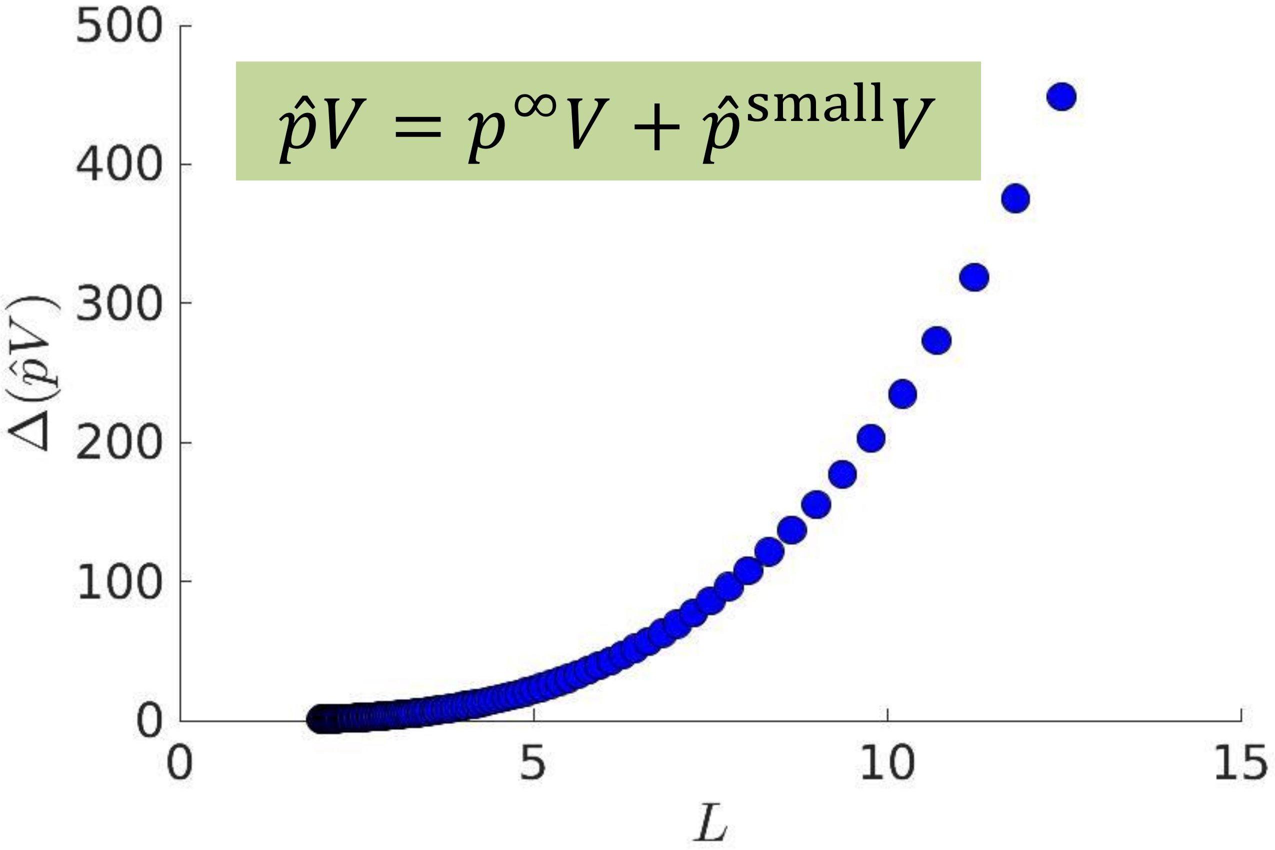


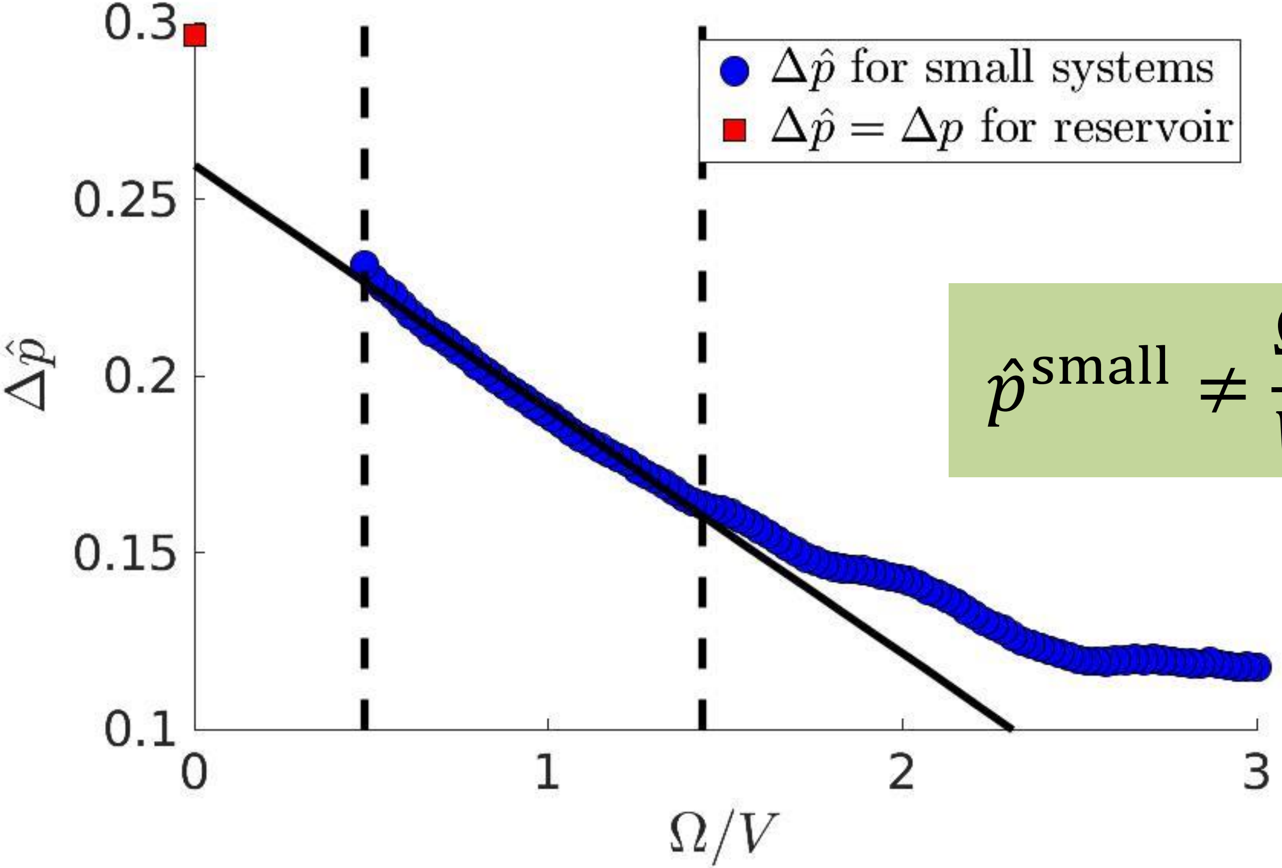
$$\frac{1}{\beta}\ln\frac{P(N|\mu_2,T,V)}{P(N|\mu_1,T,V)} = -\Delta(pV) + \Delta\mu N$$



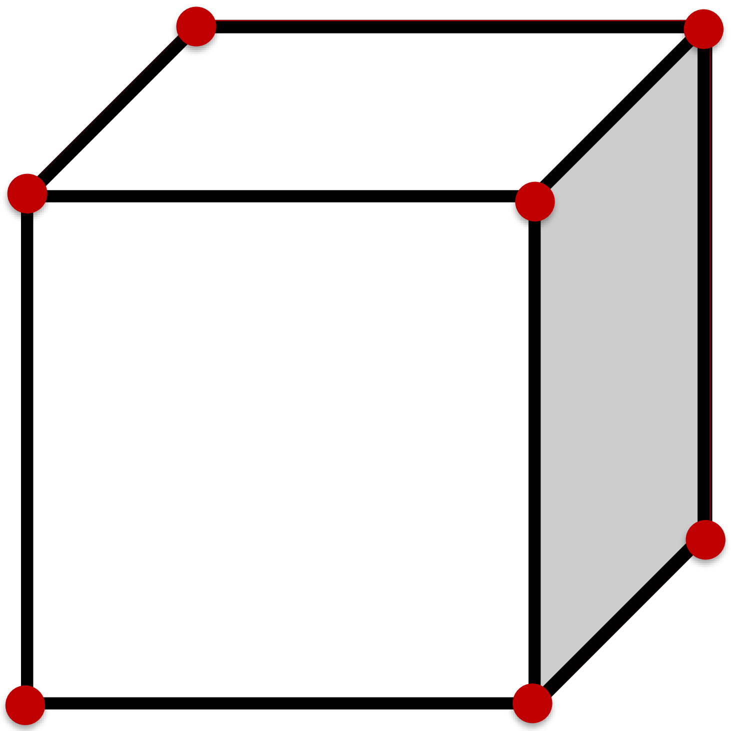
(2) Shirts MR. J Chem Theory Comput. 2013;9(2):909-926
(3) Bennett CH. J Comput Phys. 1976;22(2):245-268

$$\hat{p}V = p^{\infty}V + \hat{p}^{\mathrm{small}}V$$





$$\hat{p}^{\text{small}} \neq \frac{\Omega}{V}\hat{p}^{\text{surf}}$$



Small size contributions

Surface:

$$6\varepsilon^{\text{surf}}(\rho,T)L^2$$

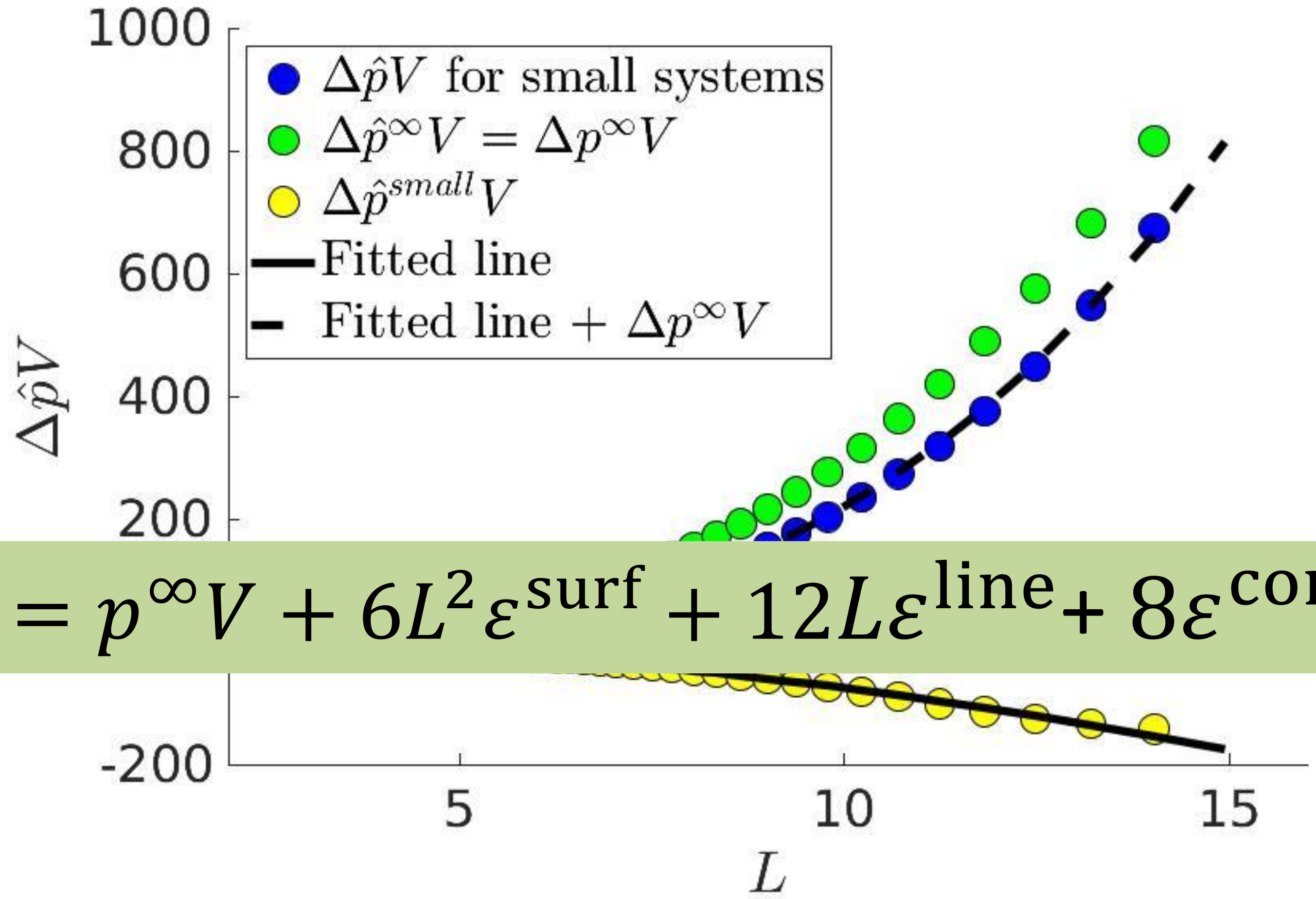
Line:

$$12\varepsilon^{\text{line}}(\rho,T)L$$

Corner:

$$8\varepsilon^{\text{corner}}(\rho,T)$$

$$\hat{p}^{\text{small}}V = 6\varepsilon^{\text{surf}}L^2 + 12\varepsilon^{\text{line}}L + 8\varepsilon^{\text{corner}}$$



$$\hat{p}V = p^{\infty}V + 6L^2\varepsilon^{\text{surf}} + 12L\varepsilon^{\text{line}} + 8\varepsilon^{\text{corner}}$$

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$\varepsilon^{\text{surf}}$, $\varepsilon^{\text{line}}$ and $\varepsilon^{\text{corner}}$ dependency on T and ρ

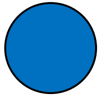
$$S^{\text{small}} = \left(\frac{\partial \hat{p}^{\text{small}} V}{\partial T}\right)_{\mu,V}$$

$$p^{\text{small}} = \left(\frac{\partial \hat{p}^{\text{small}} V}{\partial V}\right)_{\mu,T}$$

$$N^{\text{small}} = \left(\frac{\partial \hat{p}^{\text{small}} V}{\partial \mu}\right)_{V,T}$$

EQUATION OF STATE

Equation of State

- General in terms of:
  - Shape:  ,  and 
  - Ensemble: $\mu VT, NVT$ and NpT
- Other properties accessible from differentials

$$\kappa_T^{\mathrm{small}} = -\frac{1}{\rho}\left(\frac{\partial \rho}{\partial p^{\mathrm{small}}}\right)_T$$

Challenges

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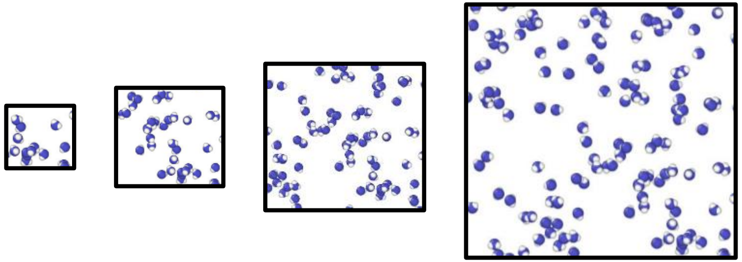

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Thank you for your attention!