Modelowanie zjawiska kondensacji kapilarnej w materiałach porowatych

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Capillary condensation in cylindrical pores: Monte Carlo study of the interplay of surface and finite size effects

A. Winkler, D. Wilms, P. Virnau, and K. Binder

Citation: J. Chem. Phys. **133**, 164702 (2010); doi: 10.1063/1.3502684

Capillary condensation of adsorbates in porous materials

Toshihide Horikawa, D.D. Do *, D. Nicholson

Advances in Colloid and Interface Science 169 (2011) 40–58

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Effect of Pore Size on the Condensation/Evaporation Transition of Confined Water in Equilibrium with Saturated Bulk Water

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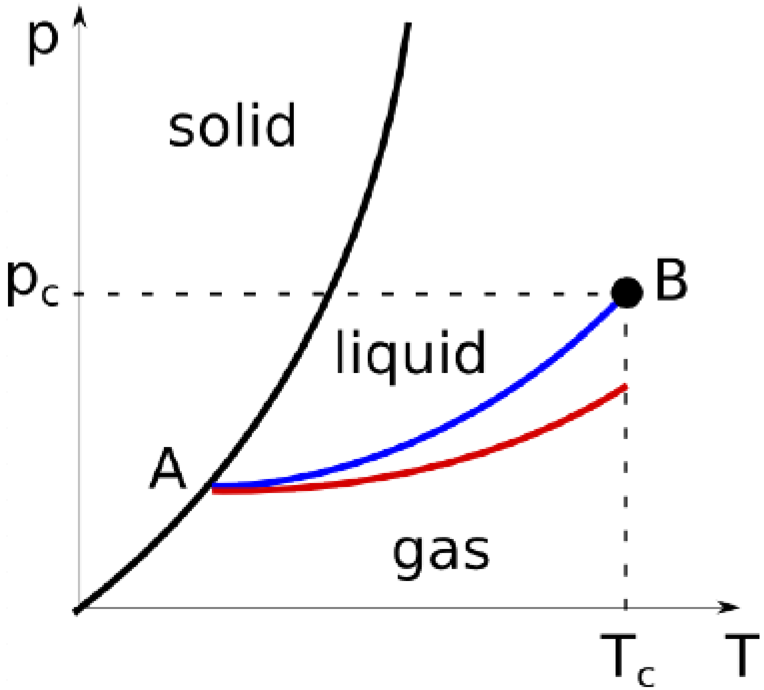


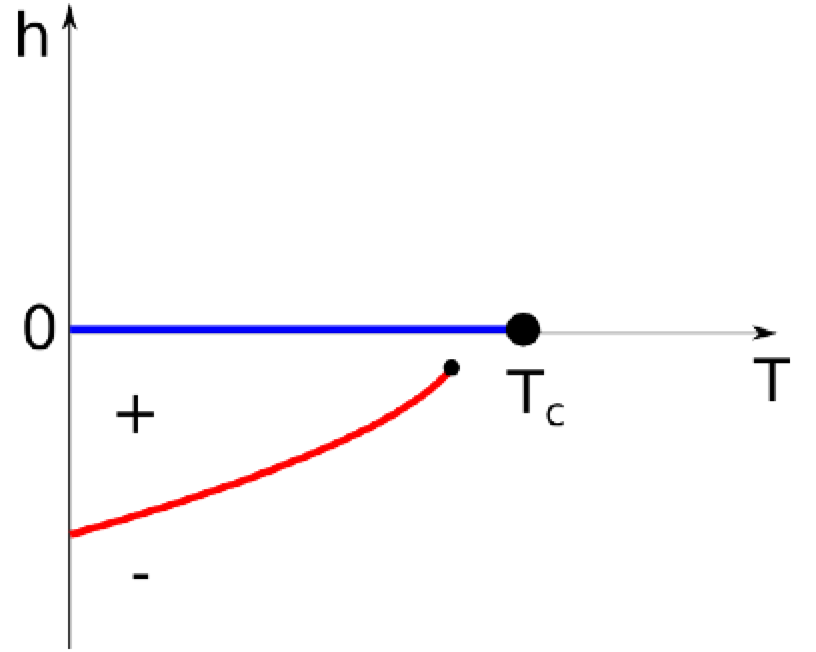
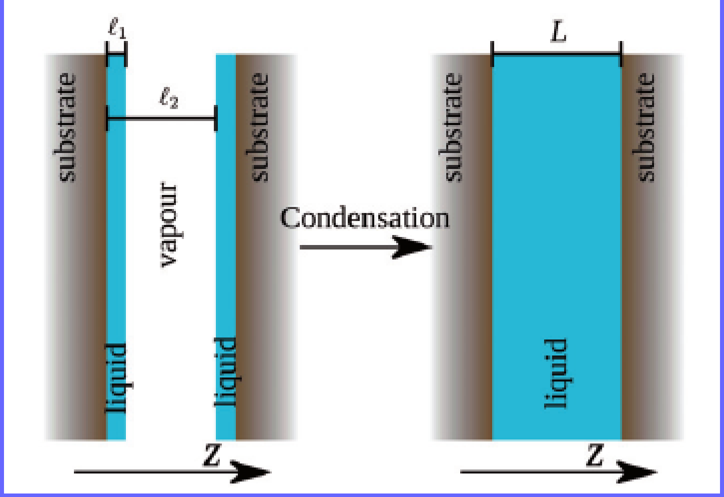
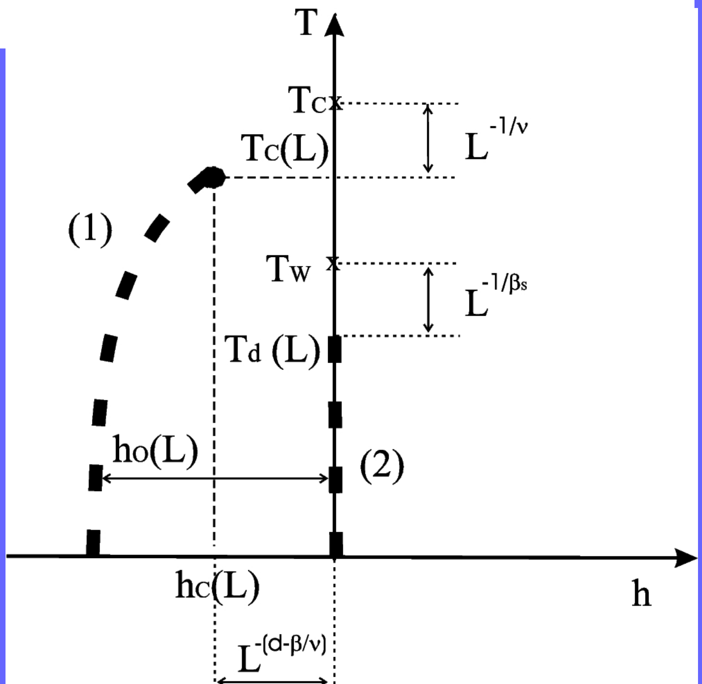


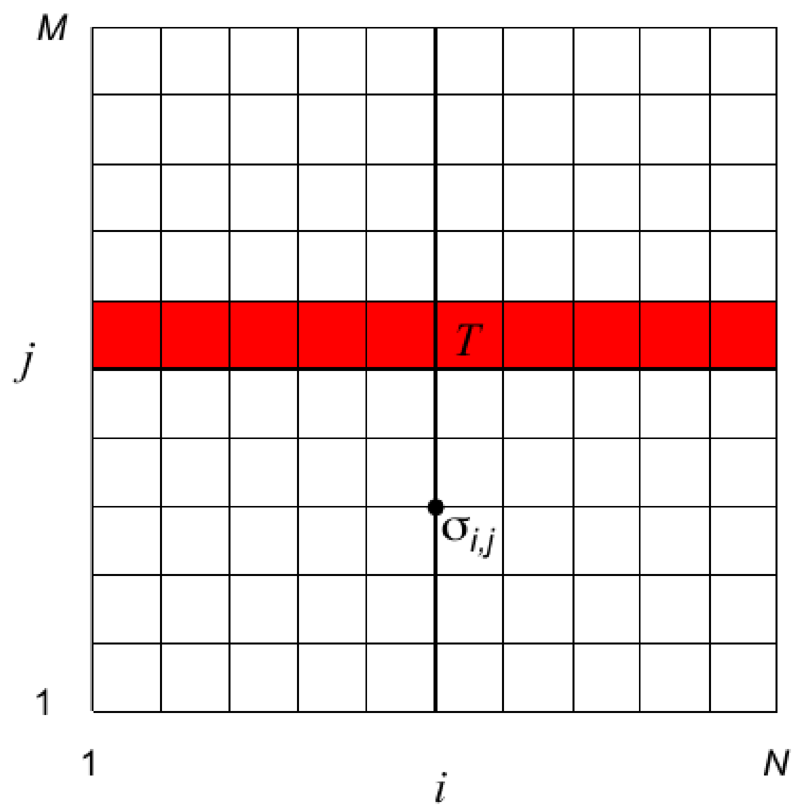
Diagram fazowy





Statistical mechanics of 2D classical spin systems on square lattice $N \times M$

Partition function Z is evaluated by means of the transfer matrix $T = \exp(-H / k_B T)$:



$$Z = \sum_{\{\sigma\}} \prod_{j=1}^{M} T\left(\sigma_{1,j} \cdots \sigma_{N,j} \mid \sigma_{1,j+1} \cdots \sigma_{N,j+1}\right)$$

$$= \sum_{\{\sigma\}} \prod_{j=1}^{M} U^T \Lambda U$$

$$= \mathrm{Tr}\left(U^T \Lambda U\right)^M = \mathrm{Tr}\,\Lambda^M$$

$$= \sum_{k=1}^{2^N} \lambda_k^M$$

$$= \lambda_1^M \left[1 + \left(\frac{\lambda_2}{\lambda_1}\right)^M + \left(\frac{\lambda_3}{\lambda_1}\right)^M + \cdots + \left(\frac{\lambda_{2^N}}{\lambda_1}\right)^M\right]$$

$$\lambda_1 > \lambda_2 \geq \lambda_3 \geq \cdots \geq \lambda_{2^N}$$

$$f = \lim_{M\to\infty} \frac{F}{M} = -k_B T \lim_{M\to\infty} M^{-1} \ln Z$$

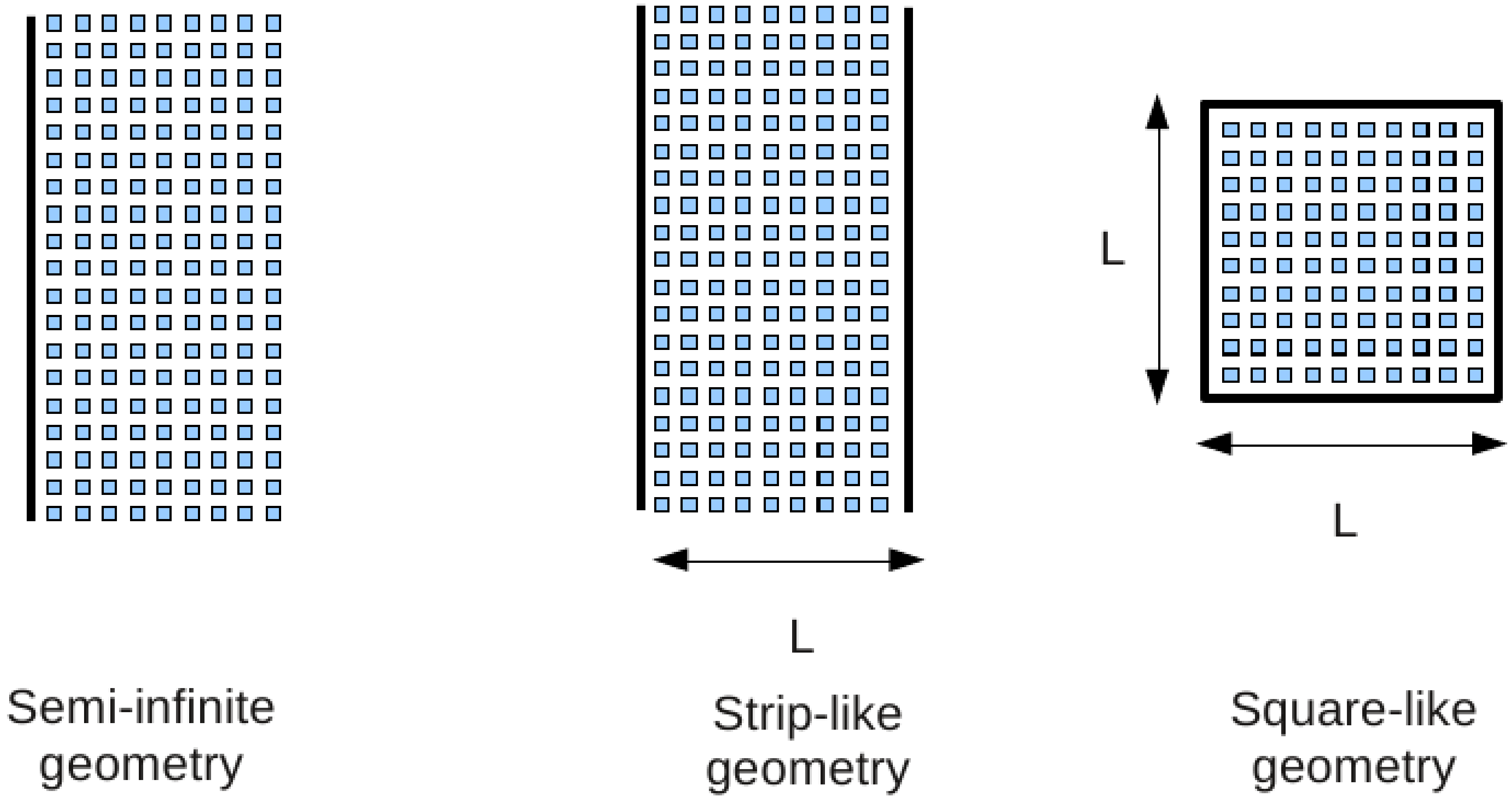
$$= -k_B T \ln \lambda_1 - \lim_{M\to\infty} \frac{k_B T}{M} \ln \left[1 + \underbrace{\left(\frac{\lambda_2}{\lambda_1}\right)^M + \left(\frac{\lambda_3}{\lambda_1}\right)^M + \cdots + \left(\frac{\lambda_{2^N}}{\lambda_1}\right)^M}_{=0 \quad \text{if} \quad \lambda_1 > \lambda_2 > \lambda_3 > \cdots > \lambda_{2^N}} \right]$$

$$= -k_B T \ln \lambda_1$$

The free energy is proportional to the largest eigenvalue of the transfer matrix, and most of the thermodynamic functions can be evaluated

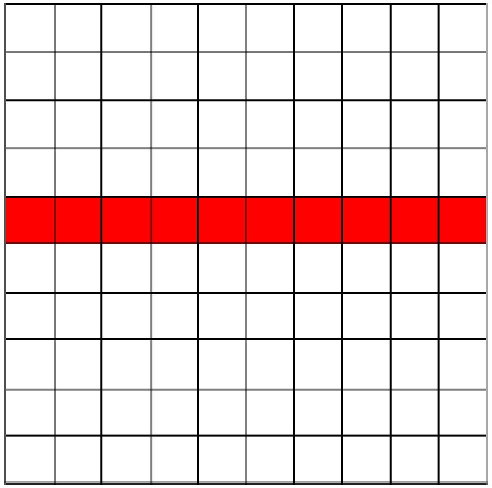
$$U \propto T^2 \frac{\partial f/T}{\partial T} \qquad M \propto \frac{\partial f}{\partial H}$$

$$C \propto \frac{\partial U}{\partial T} \qquad \chi \propto \frac{\partial f}{\partial H}$$

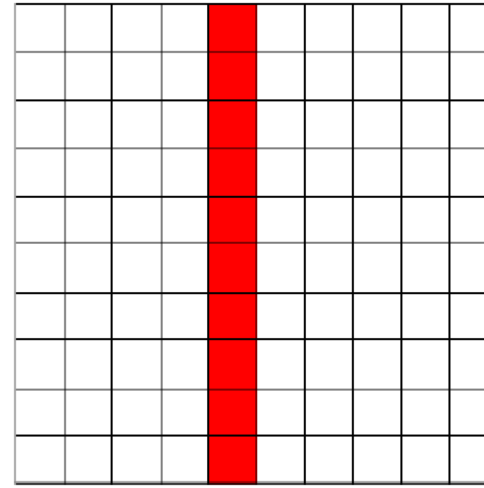

L
L
L
Semi-infinite geometry
Strip-like geometry
Square-like geometry

There are many ways how to evaluate the partition function

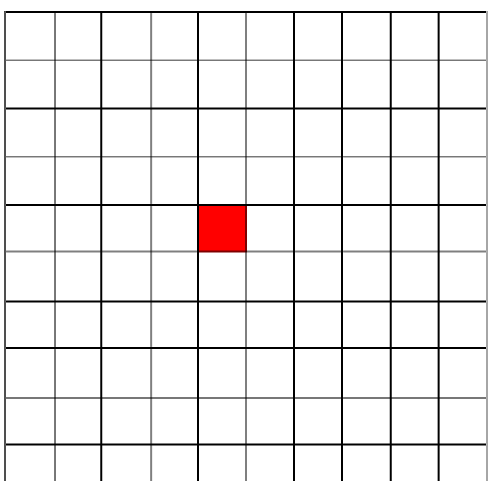
(1) $$Z = \sum_{\{\sigma\}} \prod_{j=1}^{M} T\left(\sigma_{1,j} \cdots \sigma_{N,j} \mid \sigma_{1,j+1} \cdots \sigma_{N,j+1}\right)$$



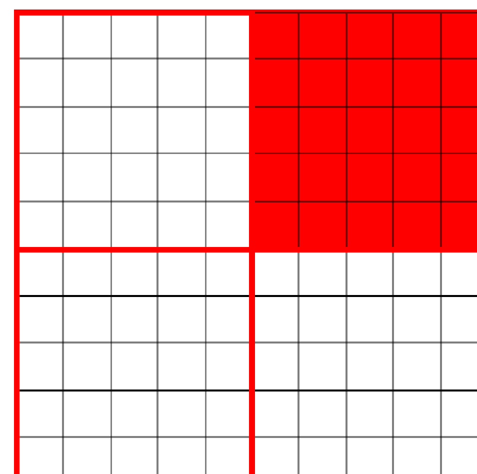
(2) $$Z = \sum_{\{\sigma\}} \prod_{i=1}^{N} T\left(\sigma_{i,1} \cdots \sigma_{i,M} \mid \sigma_{i+1,1} \cdots \sigma_{i+1,M}\right)$$



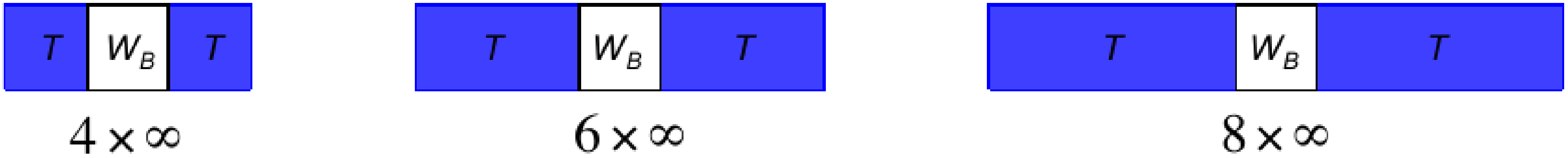
(3) $$Z = \sum_{\{\sigma\}} \prod_{i=1}^{N} \prod_{j=1}^{M} W_B\left(\sigma_{i,j}\sigma_{i+1,j} \mid \sigma_{i,j+1}\sigma_{i+1,j+1}\right)$$



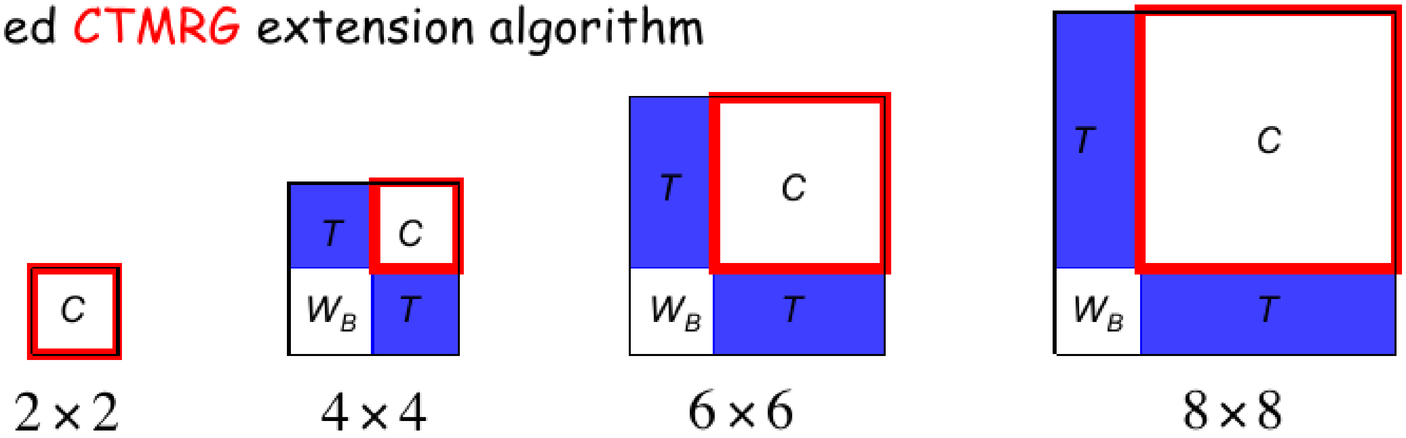
(4) $$Z = \sum_{\{\sigma\}} C\{\sigma\} \cdot C\{\sigma\} \cdot C\{\sigma\} \cdot C\{\sigma\}$$



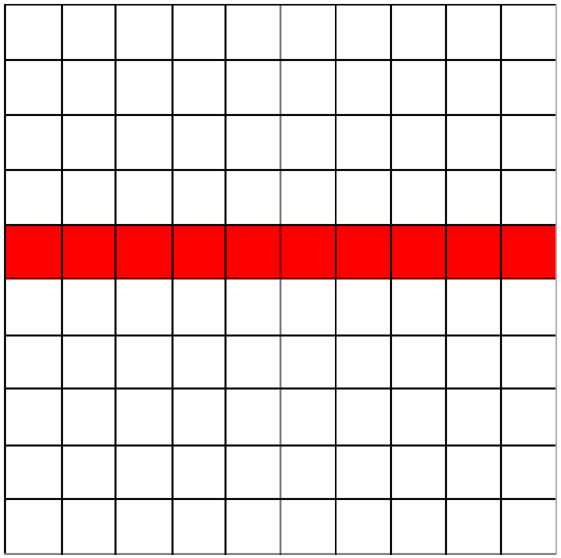
Simplified DMRG extension algorithm



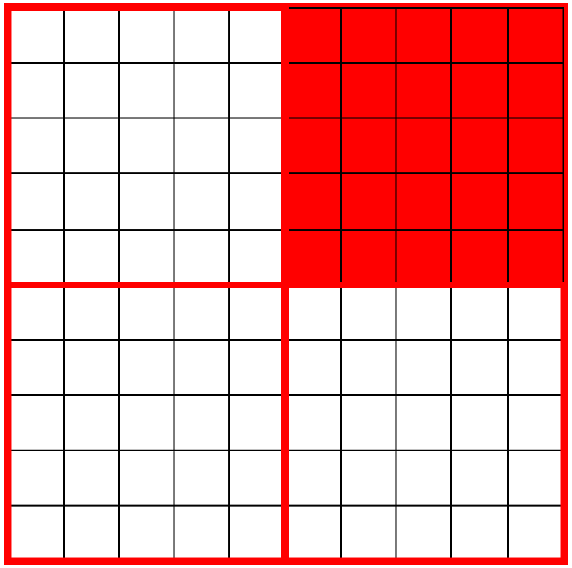
Simplified CTMRG extension algorithm



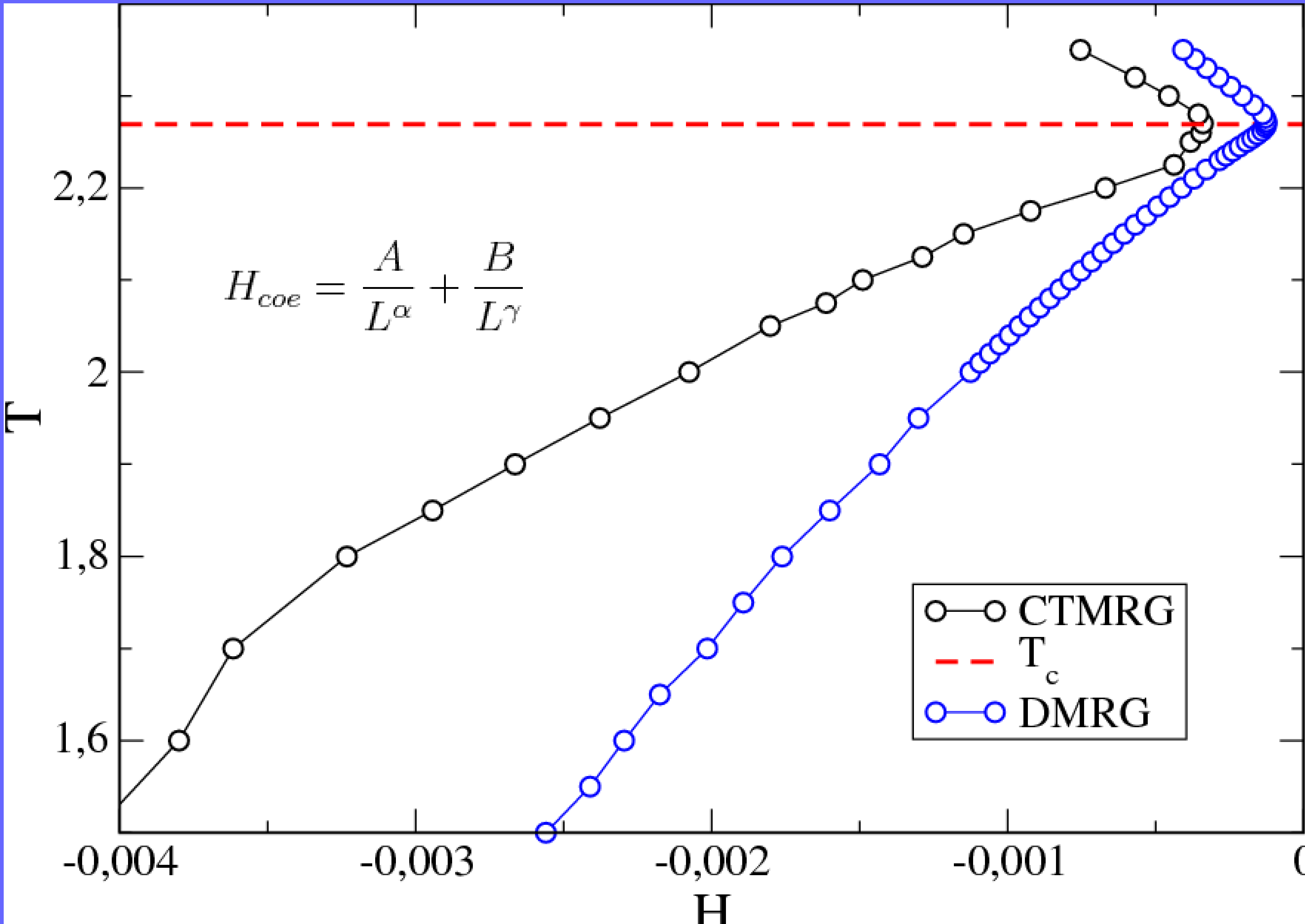
DMRG



CTMRG



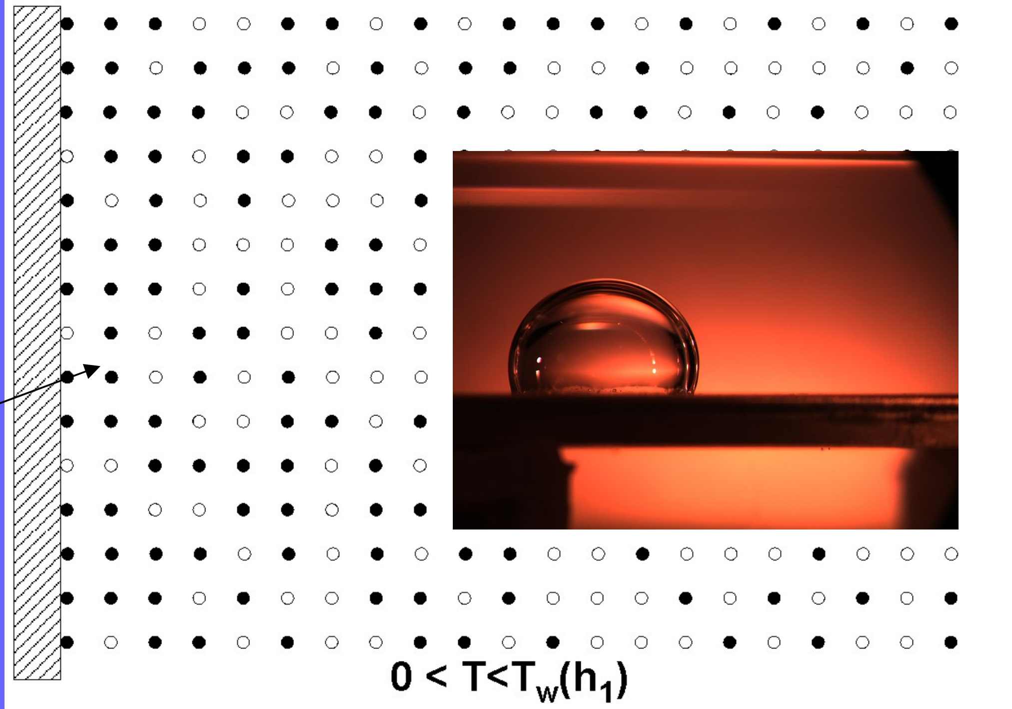
L = 500

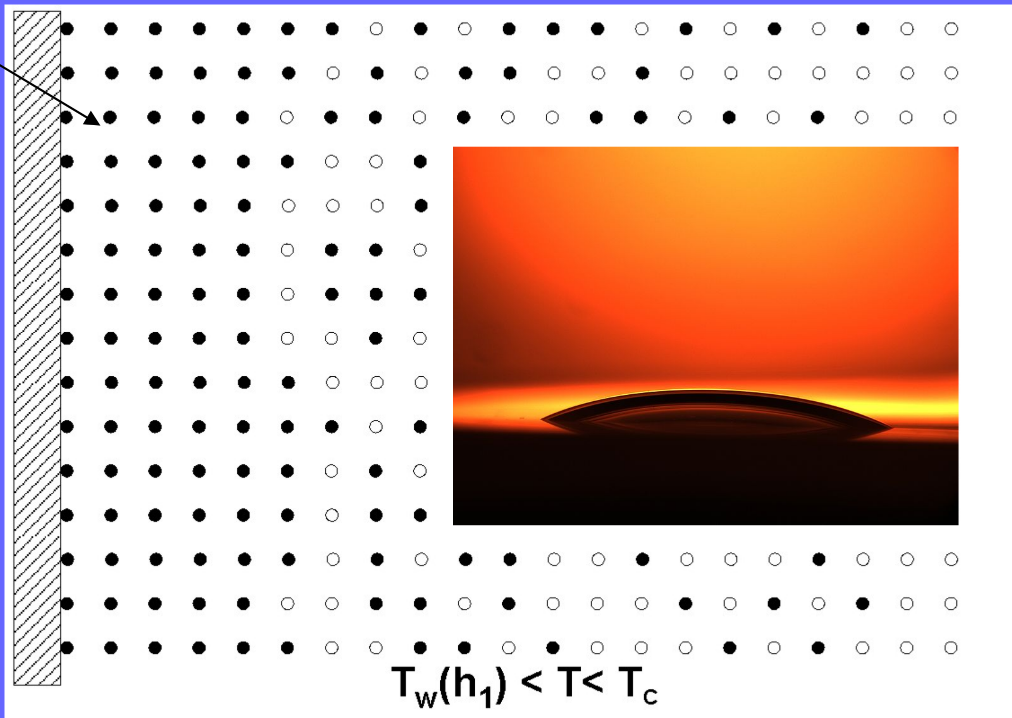


$H_{coe} = \frac{A}{L^\alpha} + \frac{B}{L^\gamma}$
CTMRG
T_c
DMRG
2,2
2
1,8
1,6
-0,004
-0,003
-0,002
-0,001
0
T
H

Zwilżanie częściowe

W pobliżu linii współistnienia !





Zwilżanie pełne

Dziękuję za uwagę