The evaporation/condensation transition of Ising droplets

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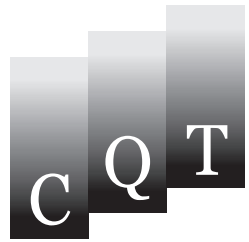


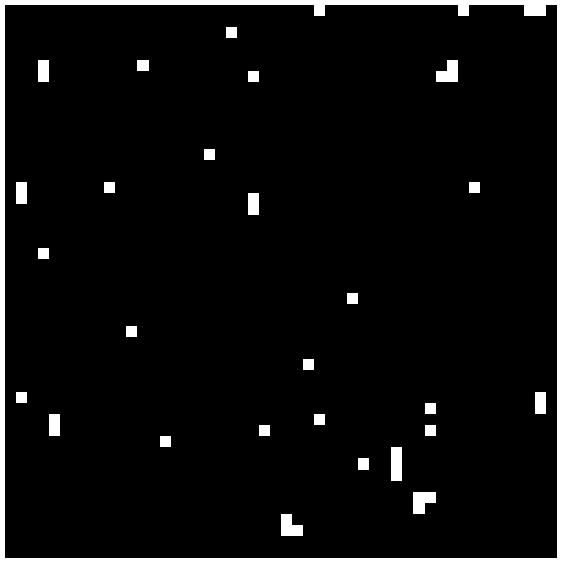
Simple argument condensation/evaporation

Only 2 contributions to the free energy are taken into account:

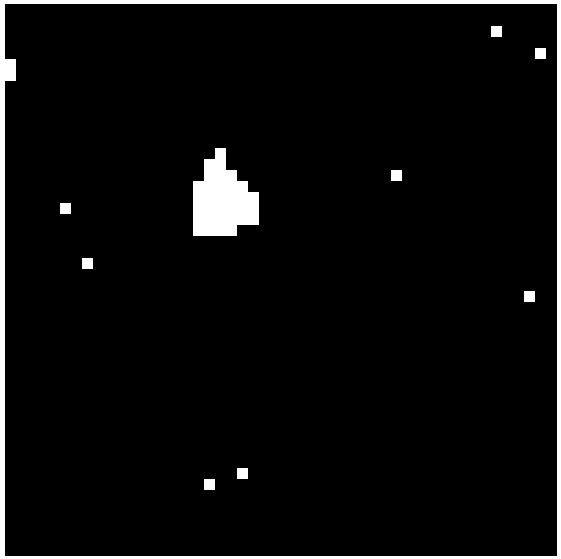
- Fluctuations
- Phase boundaries

In a purely evaporated system only fluctuations matter, in the condensed state a phase boundary exists.

Evaporated:



Condensed:



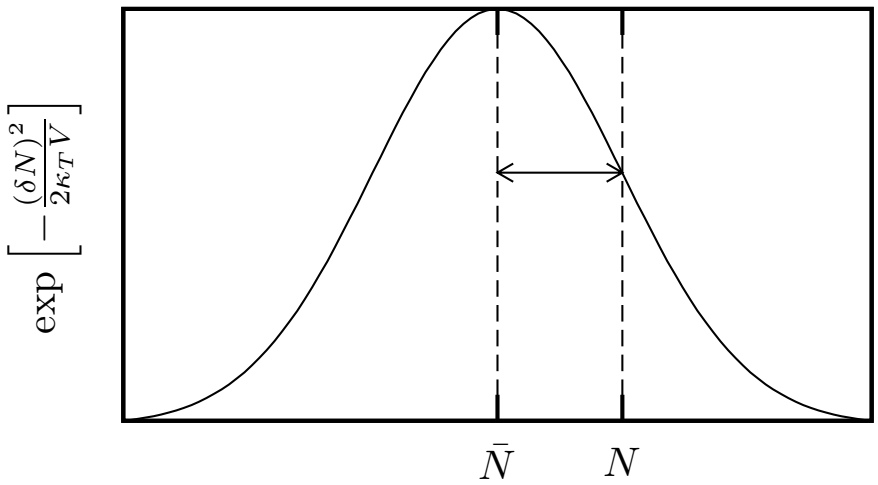
Fluctuations

Grand canonical ensemble (temperature + chemical potential fixed) with $V \sim N$ the standard deviation is

$$\Delta N \sim \sqrt{\kappa_T V}$$

Then, the probability of observing a particle excess $(\delta N) = \overline{N} - N$ has a Gaussian (central limit) distribution:

$$\exp\left[-\frac{(\delta N)^2}{2\kappa_T V}\right]$$



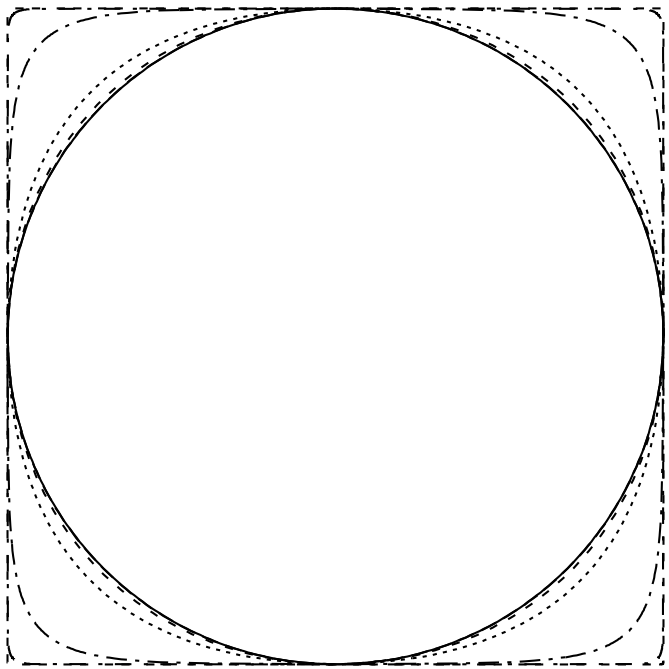
Phase boundaries

Droplet of volume δV costs:

$$\exp\left[-\tau_{\mathrm{W}} \cdot (\delta V)^{\frac{d-1}{d}}\right]$$

τ_{W}: (surface) free energy of ideal-shaped droplet of unit volume

ideal-shaped droplet: **Wulff-shape** $\Rightarrow$ minimises the (interfacial) free energy.



$T = T_{\mathrm{c}}$ ———
$T = 2.000$ – – – – –
$T = 1.500$ - - - - - -
$T = 1.000$ ·····
$T = 0.300$ –·–·–
$T = 0.050$ – ·– ·–
$T = 0.005$ -- -- --

Isoperimetric reasoning

Why does a system form a single droplet? Couldn't there be two droplet of half the volume?
A single droplet costs (in terms of interfacial length):

$$u_1 = \sqrt{4\pi V}$$

while two droplets cost

$$u_2 = 2\sqrt{4\pi \frac{V}{2}} = \sqrt{2}\sqrt{4\pi V} \qquad \text{and } n \text{ droplets} \qquad u_n = \sqrt{n}\sqrt{4\pi V}$$

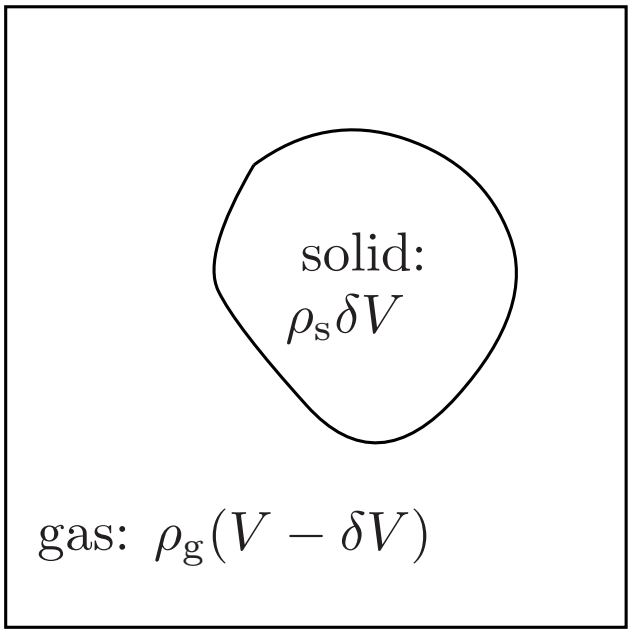
Answer: to form n droplet of total volume V costs $\sqrt{n}$ more free energy than to form a single droplet of that volume.

Non isoperimetric reasoning

Why would a system want to form a gas if a liquid (one droplet) costs much less free energy?
Answer: lots of small fluctuations have a large entropy

Location of the transition

Simple situation:



- V: volume of the system (droplet+background)
- δV: volume of the droplet
- $V - \delta V$: volume of the background
- ρ_s: density of the solid phase (droplet)
- ρ_g: density of the gaseous phase (background)

System has fixed excess δN of particles above ambient gas density.

$$\delta N = N_{\text{gas+solid}} - N_{\text{gas}} = (V - \delta V)\rho_g + \delta V \rho_s - V\rho_g = \delta V(\rho_s - \rho_g)$$

Comparing: $\frac{\text{free energy flucutations}}{\text{free energy boundary}}$

$$\frac{-(\delta N)^2/(2\kappa V)}{-\tau_{\mathrm{W}}(\delta V)^{\frac{d-1}{d}}} = \frac{(\delta N)^2(\delta N)^{-\frac{d-1}{d}}(\rho_{\mathrm{s}}-\rho_{\mathrm{g}})^{\frac{d-1}{1}}}{2\kappa\tau_{\mathrm{W}}V} = \underbrace{\frac{(\delta N)^{\frac{d+1}{d}}(\rho_{\mathrm{s}}-\rho_{\mathrm{g}})^{\frac{d-1}{d}}}{2\kappa\tau_{\mathrm{W}}V}}_{\Delta} \stackrel{!}{=} 1$$

$$\delta N = \underbrace{\frac{(2\kappa\tau_{\mathrm{W}})^{\frac{d}{d+1}}}{(\rho_{\mathrm{s}}-\rho_{\mathrm{g}})^{\frac{d-1}{d+1}}}}_{\theta} V^{\frac{d}{d+1}}$$

Results:

$\delta N \gg \theta V^{\frac{d}{d+1}}$ droplet mechanism dominates

$\delta N \ll \theta V^{\frac{d}{d+1}}$ fluctuations mechanism dominates

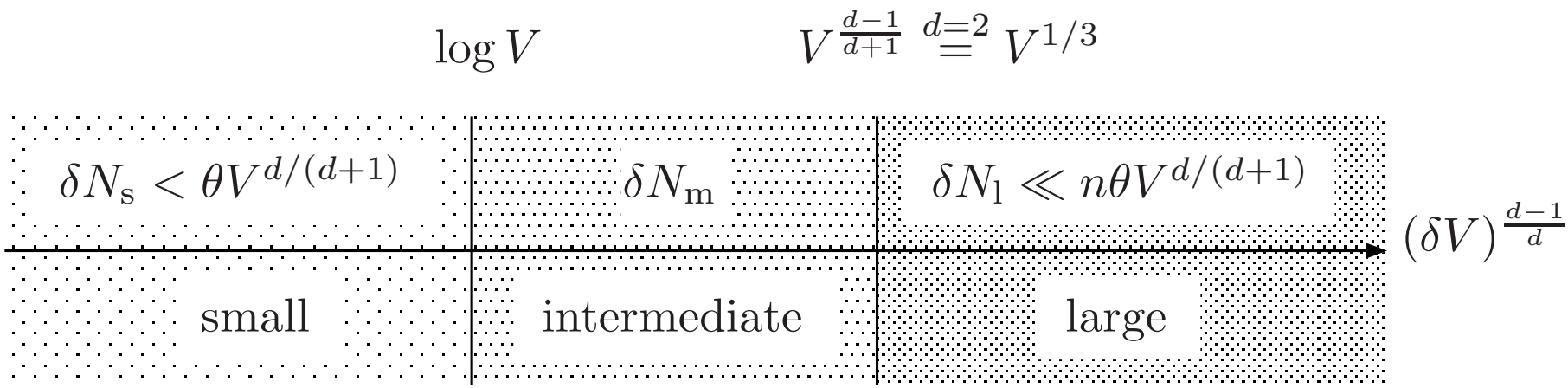
Crossover region $\delta N \approx \theta V^{\frac{d}{d+1}}$

Far away from $\theta V^{\frac{d}{d+1}}$ the behaviour is understood. But: what happens in the vicinity of the transition?

- Maybe a distribution of clusters with different sizes?
- Complicate fluctuations of the clusters?

Solution $\Rightarrow$ M. Biskup, L. Chayes and R. Kotecký, On the formation/dissolution of equilibrium droplets, *Europhys. Lett.*, 60, pp. 21-27 (2002)

Idea: divide droplets in three kinds, according to their area size



Isoperimetric reasoning (again) shows: there are no droplet of medium size, i.e. the total excess δN is divided between the droplet $\delta N_{\rm d}$ and the fluctuations $N_{\rm f}$:

$$\delta N = \delta N_{\rm d} + \delta N_{\rm f}$$

The fraction of the excess that goes into the droplet is defined as

$$\lambda = \frac{\delta N_{\rm d}}{\delta N}$$

The rest goes into the fluctuations:

$$1 - \lambda = 1 - \frac{\delta N_{\rm d}}{\delta N} = \frac{\delta N - \delta N_{\rm d}}{\delta N} = \frac{\delta N_{\rm f}}{\delta N}$$

Two different regimes:

a) $\Delta < \Delta_c$: global minimum of $\Phi_\Delta(\Delta)$ is $\lambda = 0$

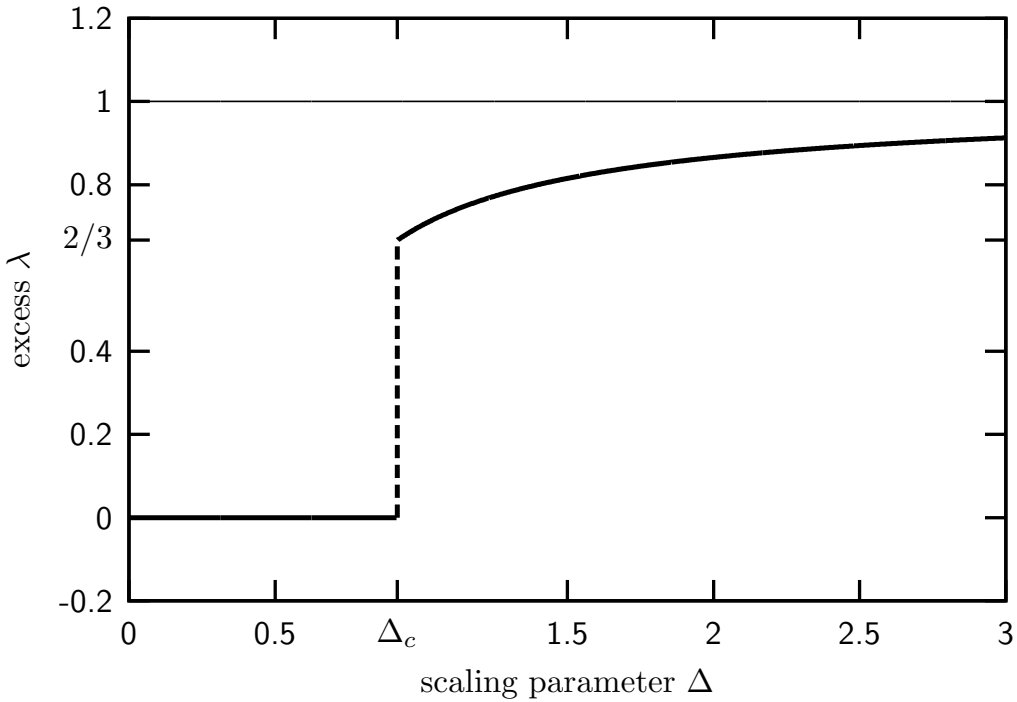
b) $\Delta > \Delta_c$: global minimum of $\Phi_\Delta(\Delta)$ is $\lambda > 0$

Results of a short calculation:

$$\lambda_c = \frac{2}{d+1}$$

and

$$\Delta_c = \frac{1}{d}\left(\frac{d+1}{2}\right)^{\frac{d+1}{d}}$$

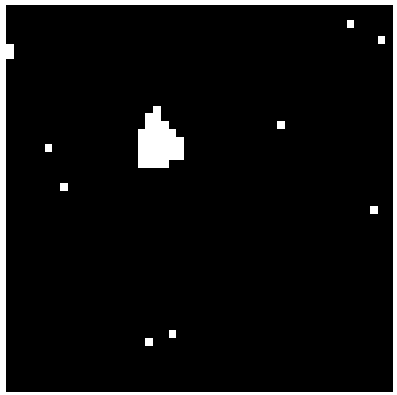


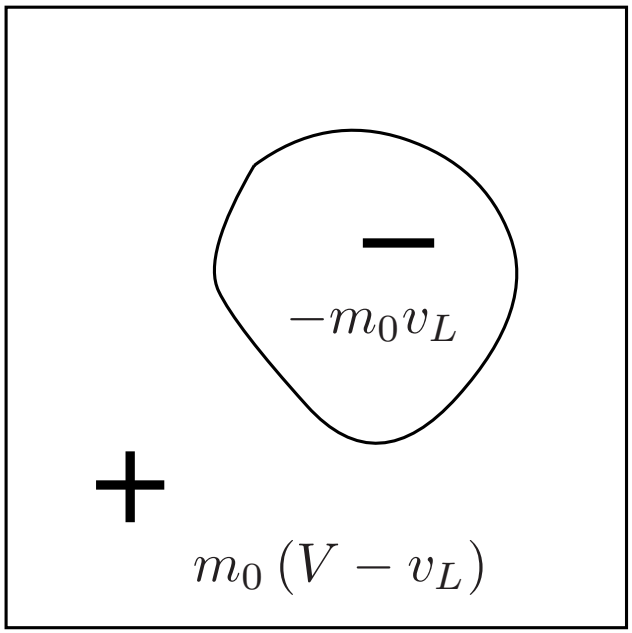
2D Ising model

To “test” the theory the most simple model is used: 2D Ising.

Interpretation: lattice-gas, i.e.

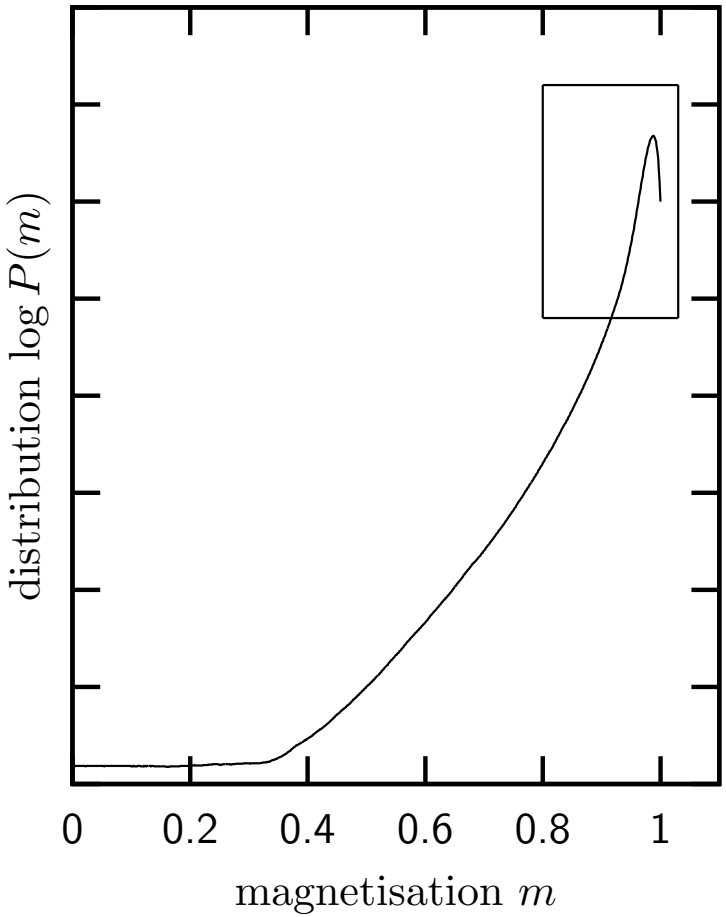
- spin up $=$ white $=$ atom
- spin down $=$ black $=$ vacancy

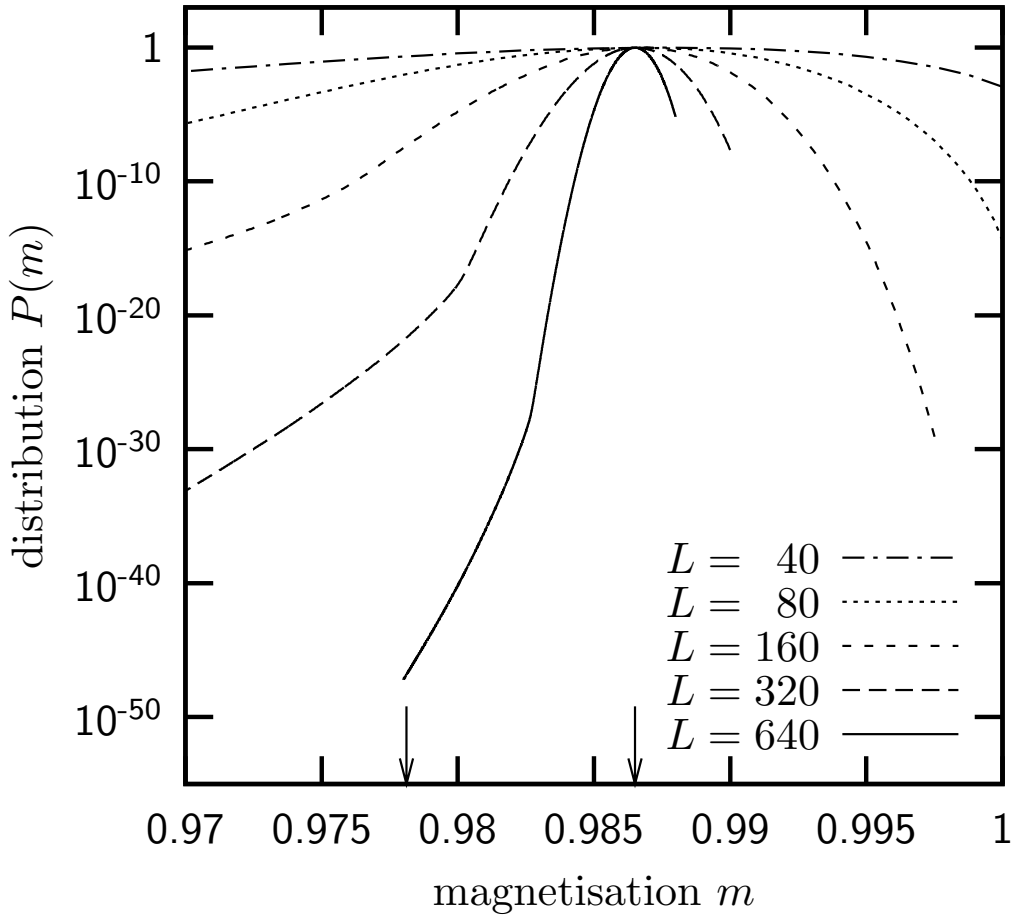




- m_0: spontaneous magnetisation (in the thermodynamic limit $L \longrightarrow \infty$)
- v_L: total excess (equivalent to δN)
- $V = L \times L$: system volume

Distribution of the magnetisation





Total magnetisation:

$$M = -m_0 \underbrace{v_L}_{\text{droplet}} + m_0 (\underbrace{V - v_L}_{\text{background}})$$

$$\Rightarrow M - V m_0 = -2 v_L m_0$$

Therefore, Gaussian fluctuations cost:

$$\exp\left[-\frac{(M-M_0)^2}{2\chi}\right] = \exp\left[-\frac{(2m_0 v_L)^2}{2\chi L 2}\right]$$

and the droplet costs:

$$\exp\left[-\tau_{\mathrm{W}}\sqrt{v_L}\right] = 2\frac{m_0^2}{\chi\tau_{\mathrm{W}}}\frac{v_L^{3/2}}{L^2}$$

Abscissa parameter:

$$\Delta_L = \frac{(2m_0 v_L)^2/(2\chi L^2)}{\tau_{\mathrm{W}}\sqrt{v_L}} = 2\frac{m_0^2}{\chi\tau_{\mathrm{W}}}\frac{v_L^{3/2}}{L^2} \quad \Rightarrow \quad \Delta = 2\frac{m_0^2}{\chi\tau_{\mathrm{W}}}\lim_{L\to\infty}\frac{v_L^{3/2}}{L^2}$$

Simulation

1.) The value v_L is fixed

2.) v_L plus the "known constants" m_0, χ, τ_W yield a value for $\Delta(m_0, \chi, \tau_W, v_L)$.

3.) A simulation at

$$M = -m_0 v_L + m_0(V - v_L) \quad \Rightarrow \quad M = m_0 V \left(1 - 2\frac{v_L}{V}\right)$$

is performed measuring λ_Δ

Problems:

- In most cases the values of m_0, χ and τ_W are unknown. Special case: 2D Ising – lots of analytic results.
- M is only valid at discrete values $\Rightarrow$ instead of fixing v_L the value of M is fixed and v_L is calculated as

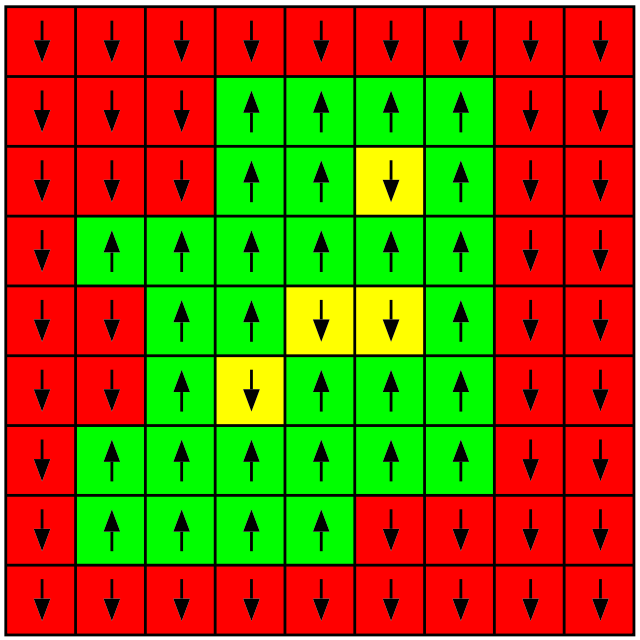
$$v_L = \frac{1}{2}\left(V - \frac{M}{m_0}\right)$$

- It is enough to use a simple Metropolis algorithm.
- To fulfil the constrain $M = \text{const.}$ Kawasaki dynamics is used.
- To measure

$$\lambda = \frac{\Omega}{v_L}$$

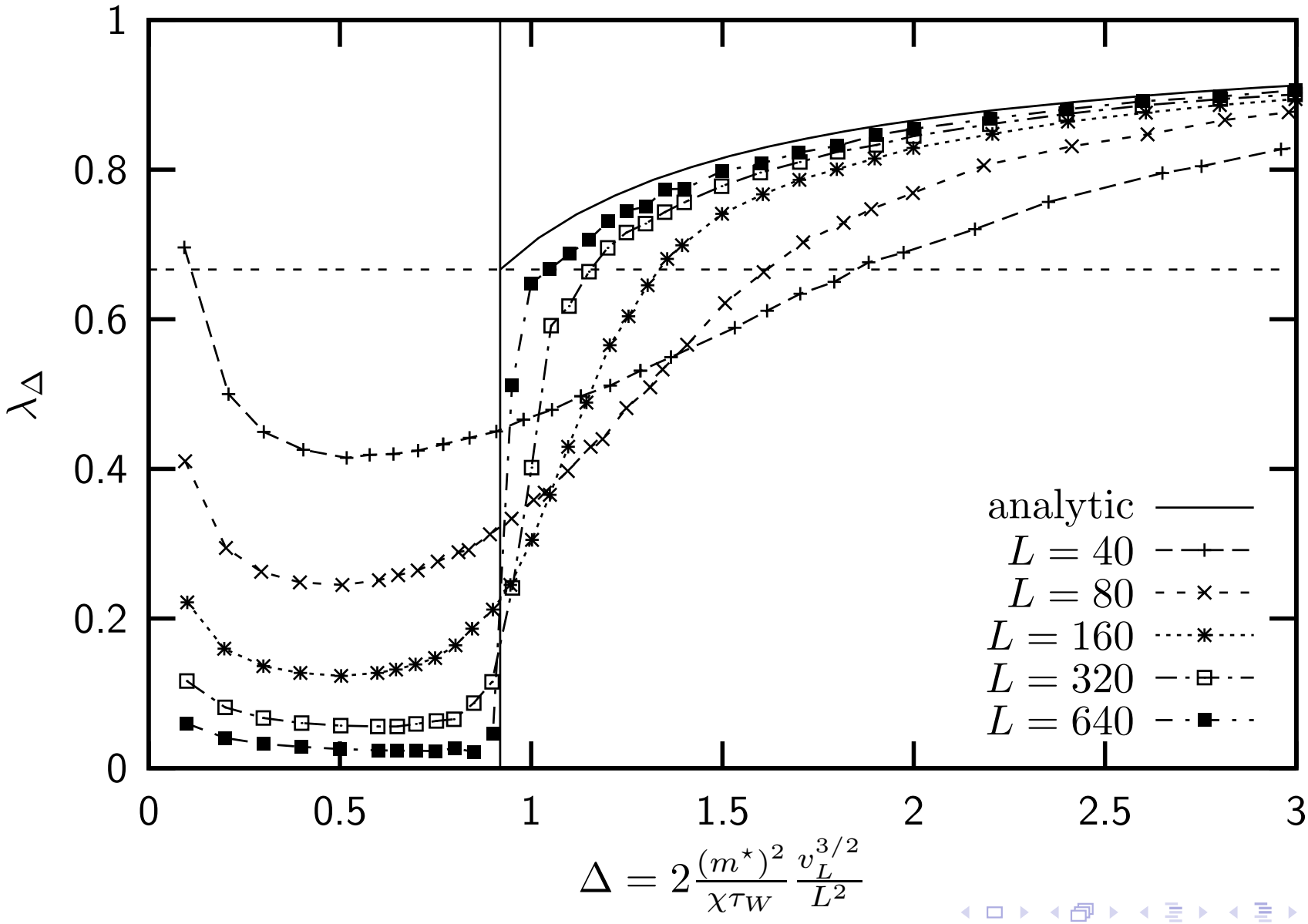
the largest droplet Ω (i.e. second largest cluster) is determined using the Hoshen-Koppelmann algorithm.

Difficulty: Ω is the area of the second largest cluster
$\Rightarrow$ What is inside and what is outside?



Main Result: λ_Δ vs Δ

2D Ising, next-neighbour, square-lattice, $T = 1.5$:



2D Ising, next-neighbour, triangular-lattice, $T = 2.4$: