The Jarzynski relation, some applications

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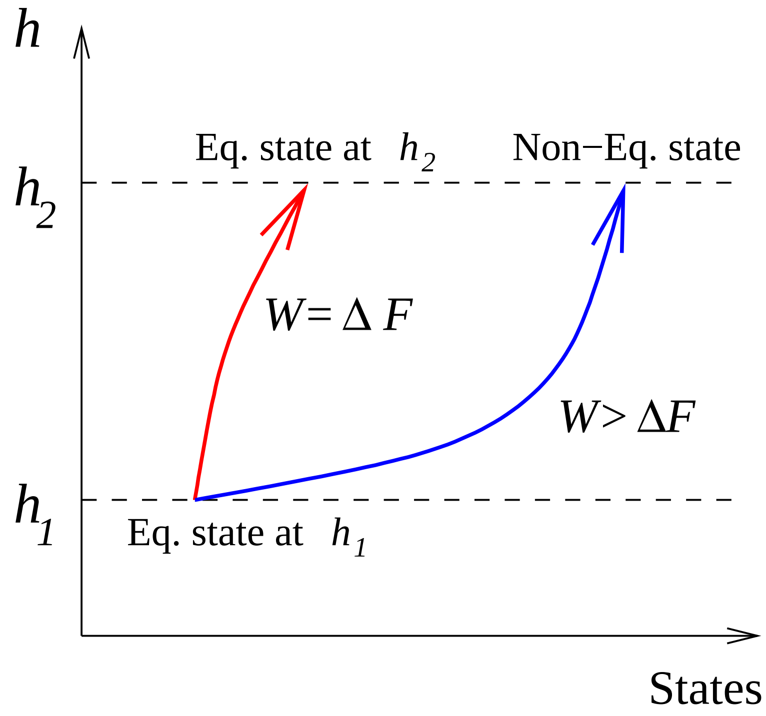
The Jarzynski relation

The system is prepared initialy at thermal and mechanical equilibrium. A work is exerted by varying an external parameter h from h_1 to h_2. The temperature is kept constant.



The Jarzynski relation states that

(1) $$\langle e^{-\beta W} \rangle = e^{-\beta\left[F(\beta,h_2)-F(\beta,h_1)\right]}$$

Two derivations: Hamiltonian dynamics, Markovian dynamics.

I. Variation of the agnetic field

- Many applications in chemistry and biophysics.
- We (Dragi and I) considered the Ising model on a square lattice

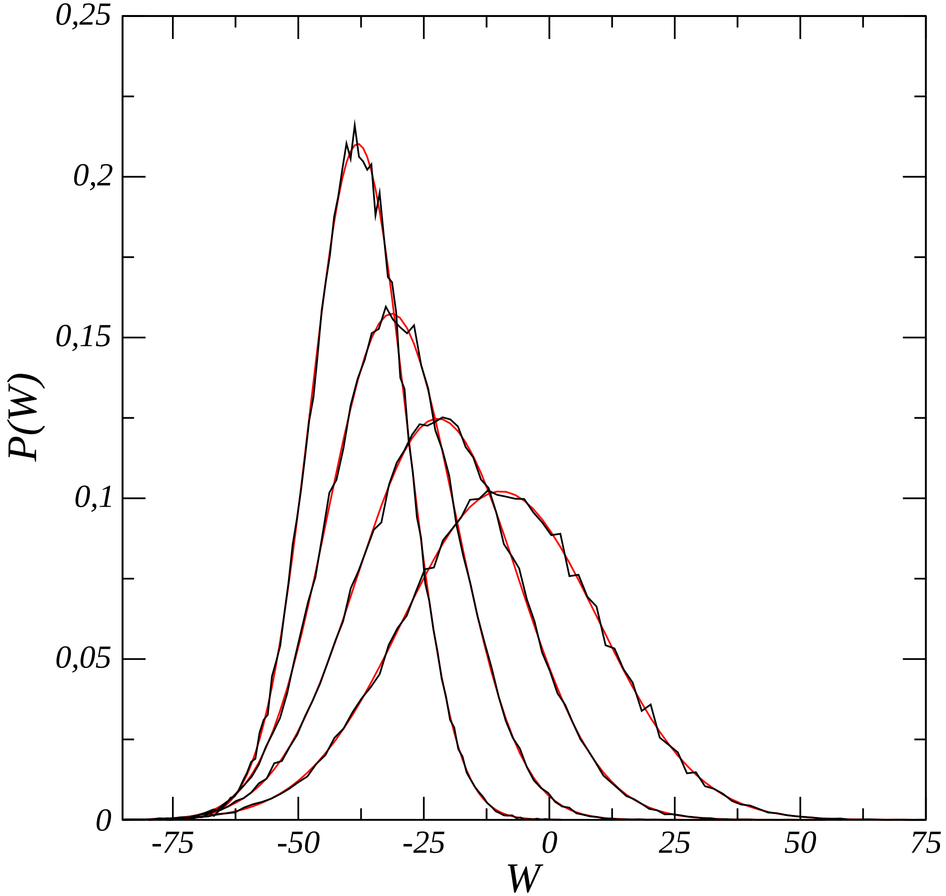
$$\mathcal{H}(\{\sigma\}) = -J \sum_{(i,j)} \sigma_i \sigma_j - h(t) \sum_i \sigma_i , \quad \sigma_i = \pm 1 \tag{2}$$

with a linearly growing magnetic field ($h(t) = \dot{h}t$). The work is

$$\begin{aligned} W &= -\int_0^h M(h) dh' \\ &= -\dot{h} \int_0^t M(t') dt' \\ &\longrightarrow -\frac{h}{n_{\text{iter}}} \sum_{i=1}^{n_{\text{iter}}} M_i \end{aligned} \tag{3}$$

The paramagnetic phase

$\beta J = 0.2$ ($< \beta_c J/2$), $\beta h = 0.1$ (weak), $n_{\rm iter} = 2$ (strongly irreversible),$5, 10$ et 20



(4) $$\langle e^{-\beta W}\rangle = \frac{1}{\sqrt{2\pi\sigma_W^2}}\int e^{-\beta W-(W-\langle W\rangle)^2/2\sigma_W^2}\,dW \Leftrightarrow \Delta F = \langle W\rangle - \frac{\sigma_W^2}{2k_BT}.$$

The paramagnetic phase [2]

N Ising domains with average magnetization m :

(5) $$\Delta F = F(h) - F(0) = -Nk_BT \ln\cosh\frac{mh}{k_BT}$$

The reversible work is

(6) $$W_{\text{rev.}} = -\dot{h}\int M_{\text{eq.}}(t')dt' = \dot{h}\int\frac{\partial F}{\partial h}(t')dt' \simeq -\frac{\dot{h}^2Nm^2}{2k_BT}t^2$$

Since the relaxtion time τ is small, the dynamical equation may be written

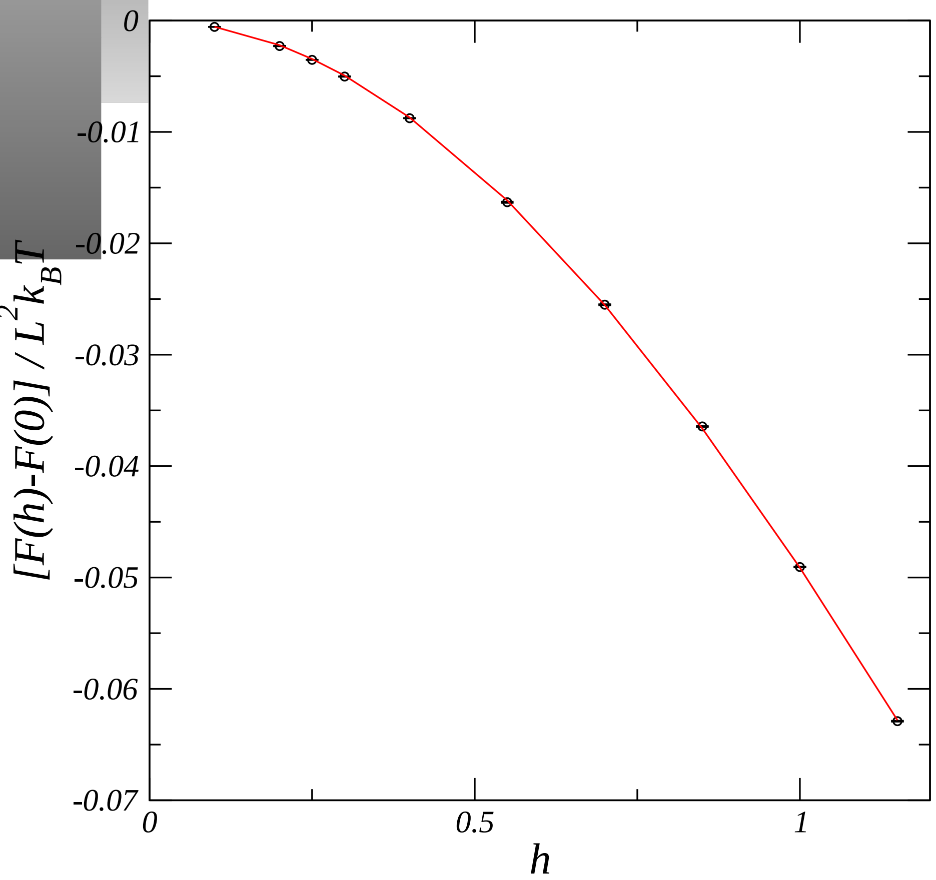
(7) $$\frac{\partial M}{\partial t} = -\frac{M(t) - M_{\text{eq.}}(h)}{\tau}$$

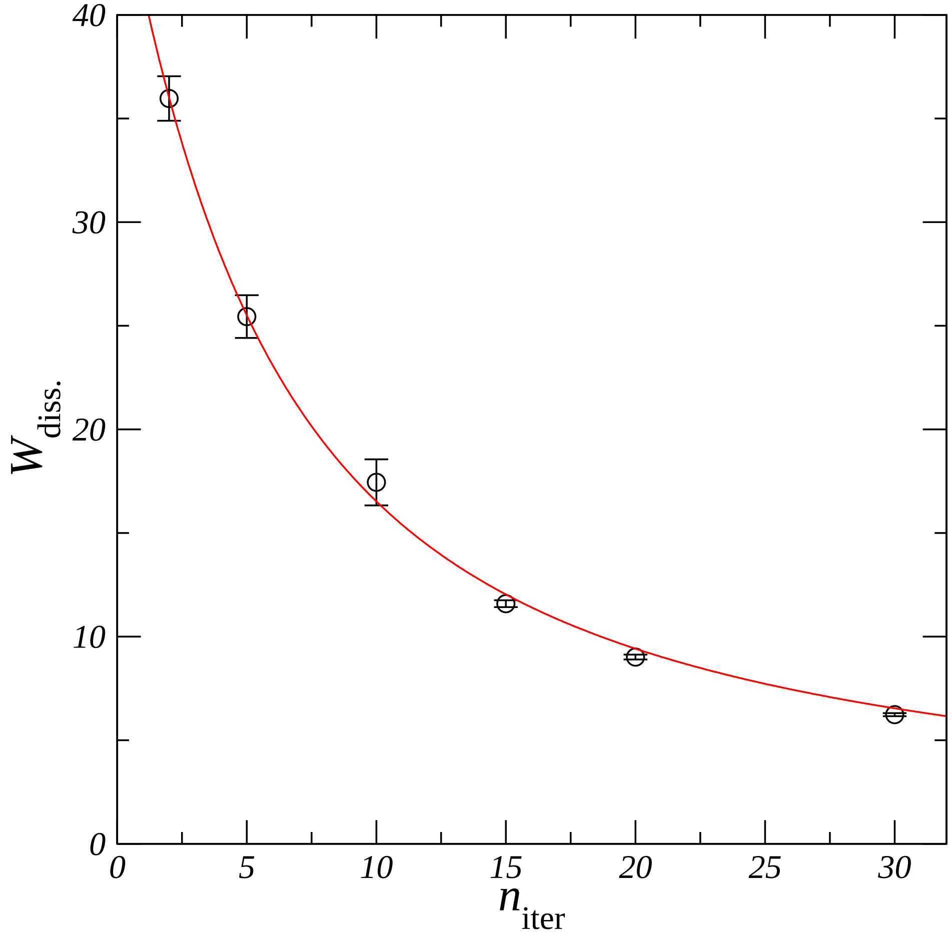
(8) $$\Leftrightarrow\ M(t) = M(0)e^{-t/\tau} + \frac{1}{\tau}\int_0^t M_{\text{eq.}}(h(t'))e^{-(t-t')/\tau}dt'$$

It leads to the dissipated work :

(9) $$W_{\text{diss.}} \simeq \dot{h}M_{\text{eq.}}(h)\tau\left[1 - \frac{\tau}{t}\left(1 - e^{-t/\tau}\right)\right]$$

The paramagnetic phase [3]





The ferromagnetic phase

The probability distribution $\wp(W)$ displays two gaussian peaks corresponding to the work exerted on the two ferromagnetic phases

$$\Delta F = -k_B T \ln \langle e^{-\beta W} \rangle \simeq -k_B T \ln \left[\frac{1}{2} e^{-\beta M_0 h} + \frac{1}{2} e^{\beta M_0 h} \right] \simeq -M_0 h + k_B T \ln 2 \tag{10}$$

with $M_0 = L^2$. The average work is

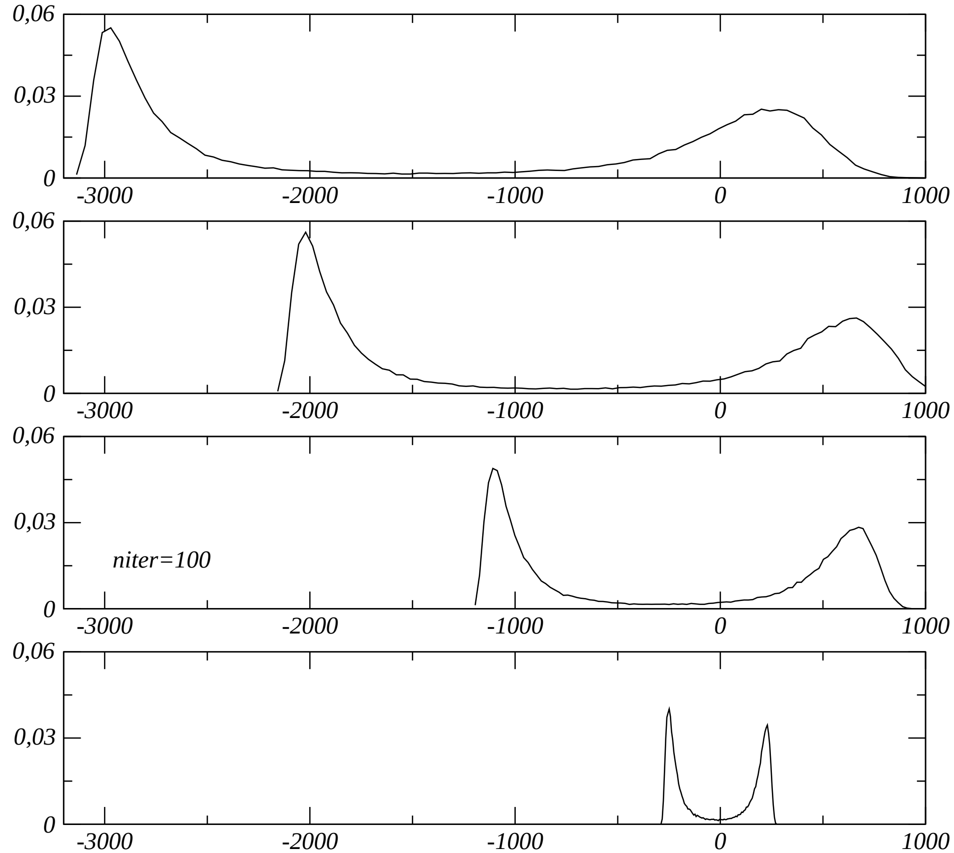
$$\langle W \rangle = (-M_0 h + M_0 h)/2 = 0 \tag{11}$$

so that the dissipated work is

$$W_{\mathrm{diss.}} = \langle W \rangle - \Delta F \simeq -\Delta F \tag{12}$$

Only the peak at $W < 0$ contributes to $\langle e^{-\beta W} \rangle$. One can calculate $W_{\mathrm{diss.}}$ using the width of this peak.

The critical point

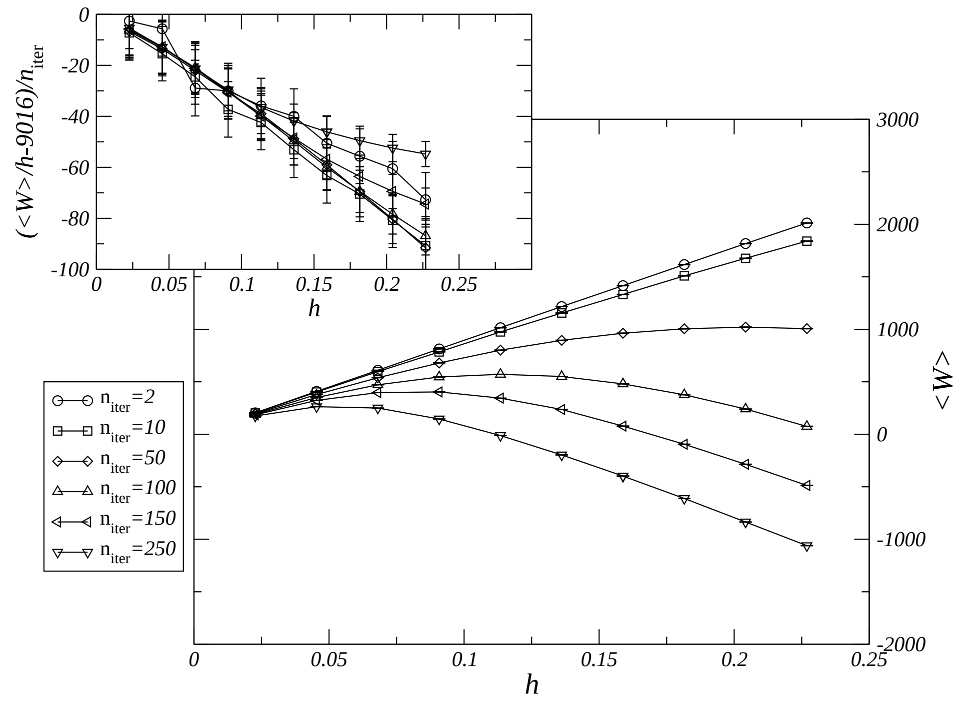


From top to bottom, the final magnetic field is $h = 0.044$, $h = 0.031$, $h = 0.017$ and 0.004 and $n_{\rm iter} = 100$ in the four cases (which means that the larger h and the faster the transformation).

The critical point [2]

(13) $$\frac{\partial M}{\partial t} = -\frac{\delta \mathcal{F}}{\delta M} \simeq \kappa h(t) \;\Leftrightarrow\; M(t) \simeq M(0) + \kappa \int_0^t h(t')dt'$$

(14) $$W = -\int_0^t M(t)\dot{h}dt = -M(0)\dot{h}t - \frac{\kappa}{6}\dot{h}^2 t^3 = -M(0)h - \frac{\kappa}{6}h^2 t$$



The critical point [3]

The Jarzynski equation gives access to critical exponents:

$$F_{\mathrm{sing.}}(h) \underset{T\to T_c,h\ll 1}{\sim} h^{1+1/\delta} \tag{15}$$

$n_{\mathrm{iter.}}$	$1+1/\delta$	δ
2	1.024(7)	42(1)
10	1.045(6)	22.2(3)
50	1.059(5)	17.0(1)
100	1.064(4)	15.7(1)
150	1.065(3)	15.36(7)
250	1.066(2)	15.13(5)

Exact value : $\delta = 15$

The average $\langle e^{-\beta W}\rangle$ is dominated by rare events when the transformation is strongly irreversible: slow convergence.

II. Variation of the temperature

Let us vary not only the magnetic field but also the temperature. This is possible only in the case of a Markovian dynamics because the interaction with the bath is taken into account by the transtion rates. On can show that the Jarzynski relation reads

$$\left\langle e^{-\int_{t_i}^{t_f}[\dot{\beta}U(\sigma(t))-\beta\dot{h}M(\sigma(t))]dt}\right\rangle = e^{-[\beta(t)F(\beta(t),h(t))]_{t_i}^{t_f}} \tag{16}$$

where

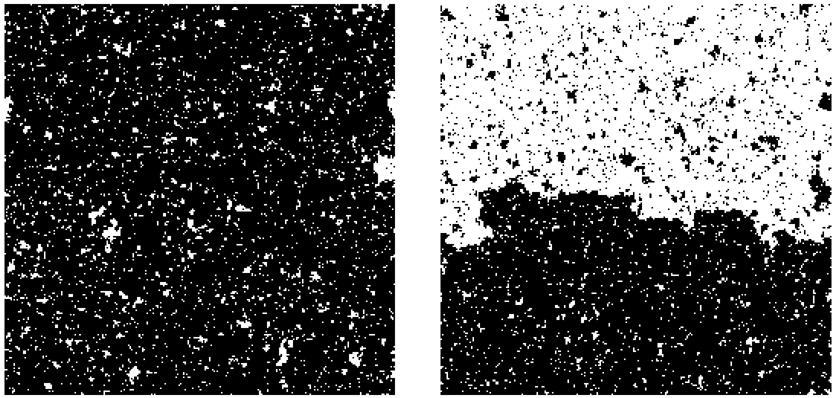
$$U(\sigma(t)) = E(\sigma(t)) - h(t)M(\sigma(t)) \tag{17}$$

“It is possible to view this change as an additional perturbation that exerts a sort of *entropic work* on the system” (Crooks)

MC calculation of the surface tension

We considered the 2D and 3D Ising model with two different boundary conditions: periodic and anti-periodic in one direction. The systems are thermalized at low temperature:

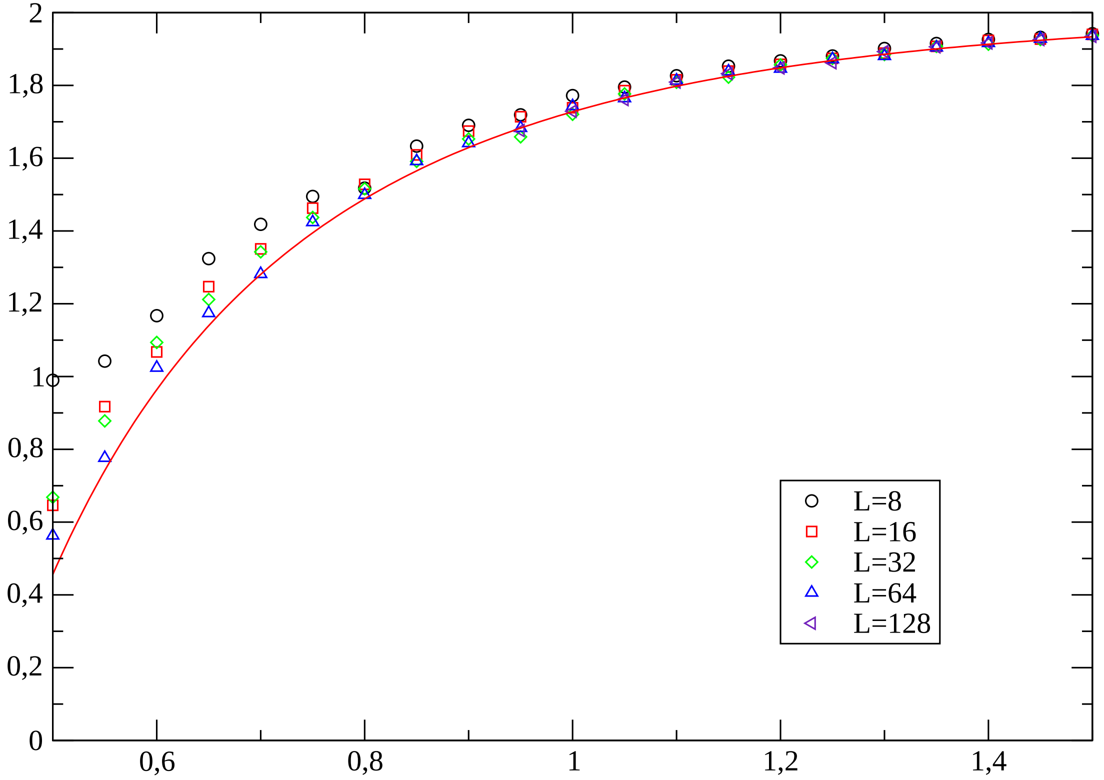
and then heated:



Surface tension of the 2D Ising model

The derivation depends only on detailled balance so we will use cluster algorithms (Swendsen-Wang and Hasenbusch-Meyer). The order-order surface tension is

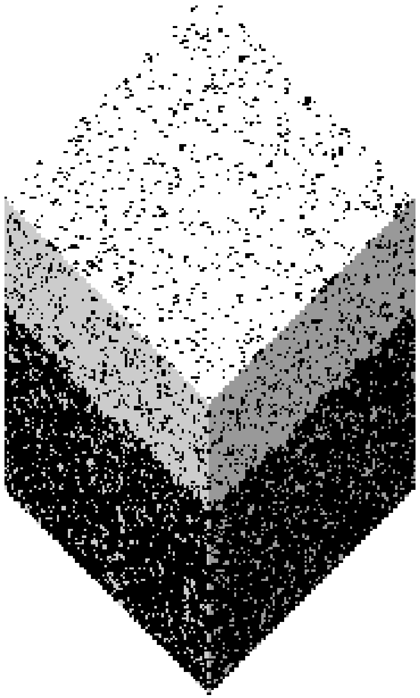
$$\sigma = \frac{1}{L}\left[F_{\mathrm{APer.}} - F_{\mathrm{Per.}}\right] \tag{18}$$

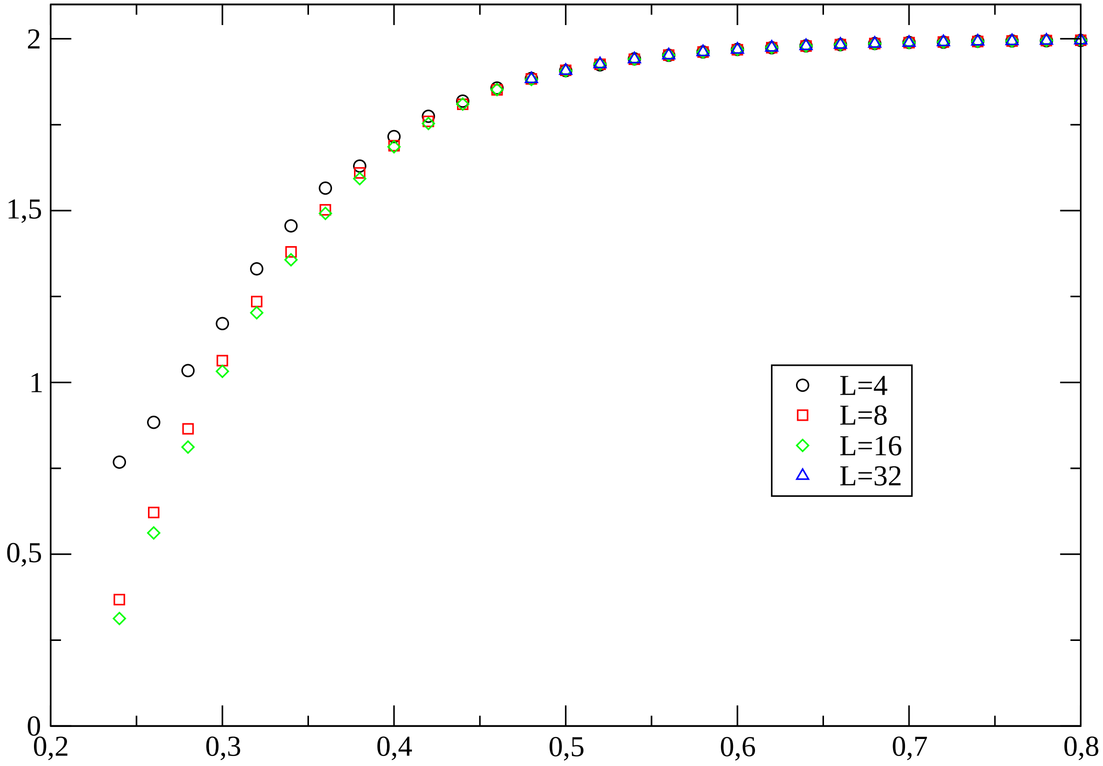


Surface tension σ versus β.

Finite-size effects are weaker with free boundary conditions.

Surface tension of the 3D Ising model





Surface tension σ versus β

Comparison with other algorithms

- Thermodynamic integration

(19) $$\beta F_s = \int_0^{\beta} \Big[U_{\text{Aper.}}(\beta') - U_{\text{Per.}}(\beta') \Big] d\beta'$$

- Snake algorithm
  Set of MC simulations at different temperatures $\{\beta_1, \beta_2, \ldots, \beta_N\}$

(20) $$\frac{\mathcal{Z}_{\beta_N}}{\mathcal{Z}_{\beta_1}} = \frac{\mathcal{Z}_{\beta_N}}{\mathcal{Z}_{\beta_{N-1}}} \cdots \frac{\mathcal{Z}_{\beta_2}}{\mathcal{Z}_{\beta_1}}$$

where each ratio is estimated by reweighting of the MC data as

(21) $$\frac{\mathcal{Z}_{\beta_{i+1}}}{\mathcal{Z}_{\beta_i}} = \langle e^{-(\beta_{i+1}-\beta_i)E} \rangle_{\beta_i}$$

Each ratio is equivalent to the Jarzynski relation with $n_{\text{niter}} = 1$.