Uma discussão sobre metaestabilidade em dinâmicas estocásticas

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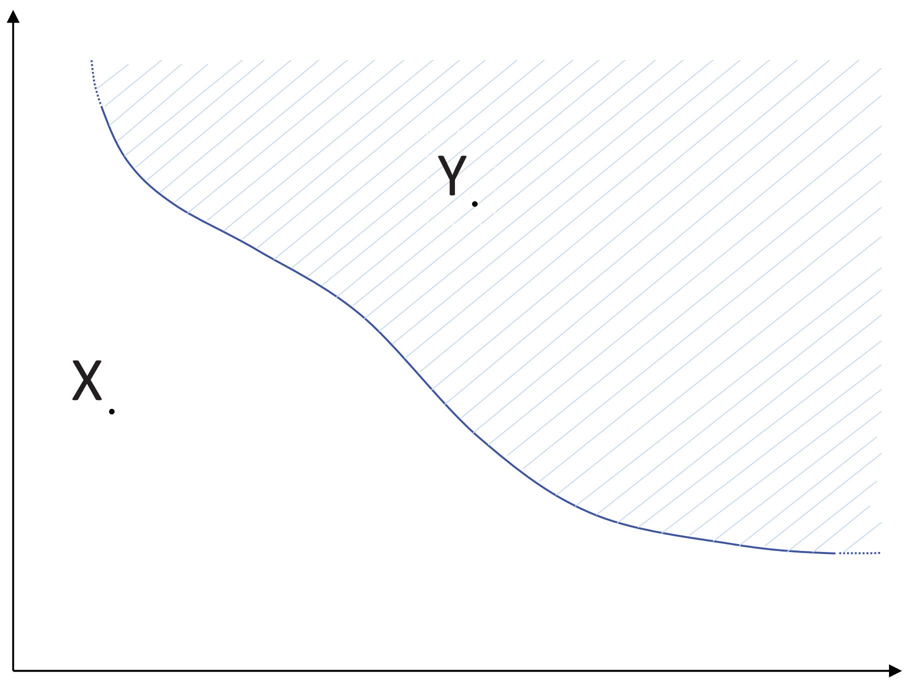
I - Discussão geral

II - Colaboração com Alexandre Gaudillière e Paolo Milanesi

Ciclo de Palestras PPGE
10/07/2024

Metastability: very frequent phenomenon for thermodynamic systems close to a first order phase transition.



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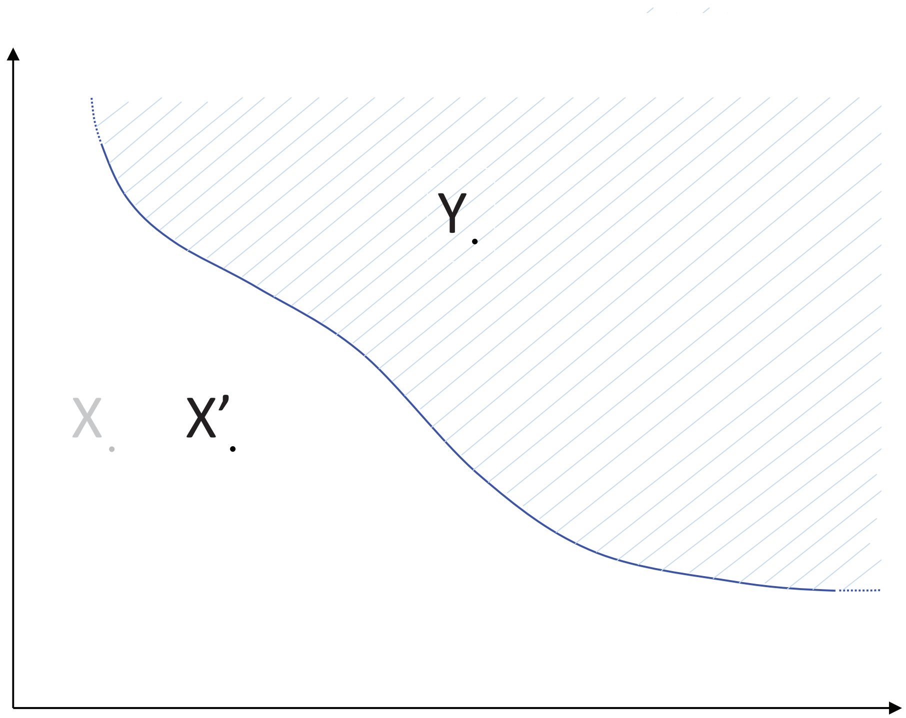
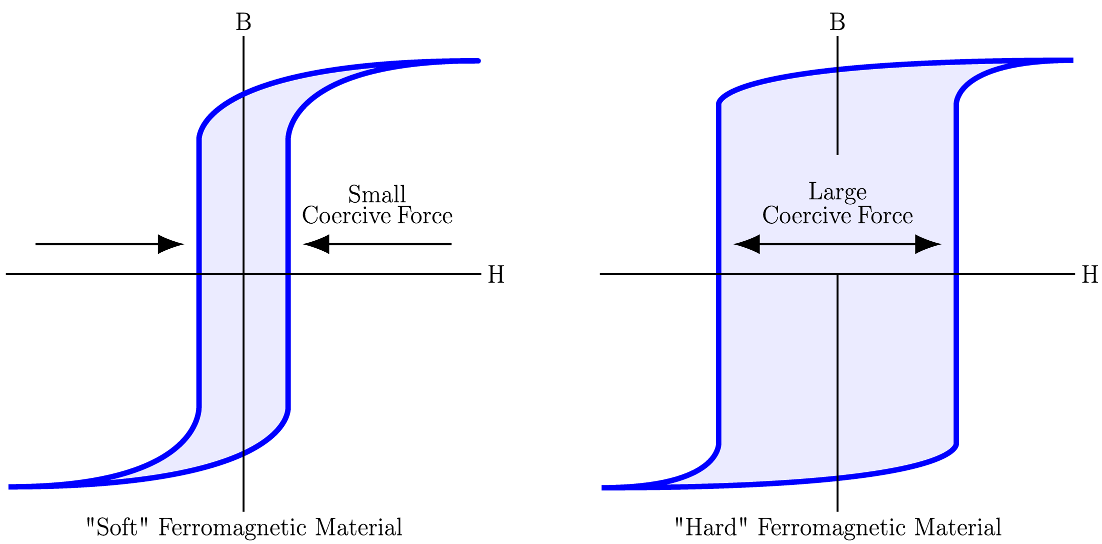


Common classical examples:

- supercooled liquids, supersaturated vapors;
- ferromagnets with magnetization opposed to the field



hysteresis loop

• From the experimental point of view, X' shares properties very similar to those of equilibrium state: "mestastable branch of isothermal curve".

• A small external perturbation /spontaneous fluctuation allows the formation of a nucleus of the new phase ("critical droplet") starting an irreversible process towards state Y.

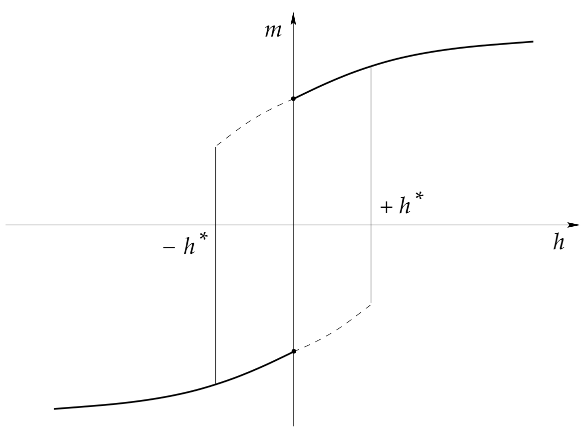
Metastability may be seen as

"The gentlest of non-equilibrium phenomena" (Gaveau, Schulman)

Natural questions:

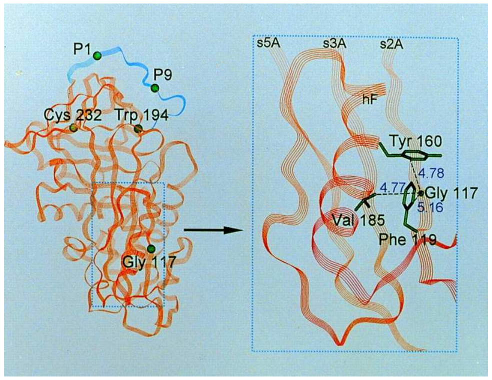
• statics: "metastable branch" ?

• dynamics: "lifetime" ?



Metastability can be observed in big variety of areas

- physics
- biology
- science of materials
- economy
- studies of climate, etc...



A first description – van der Waals - Maxwell theory (≈1870)

vapour-liquid transition

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vapour-liquid transition

(semi-phenomelogical grounds)

Starting from the equation for "perfect gas" $\mathrm{P}v = k\mathrm{T}$

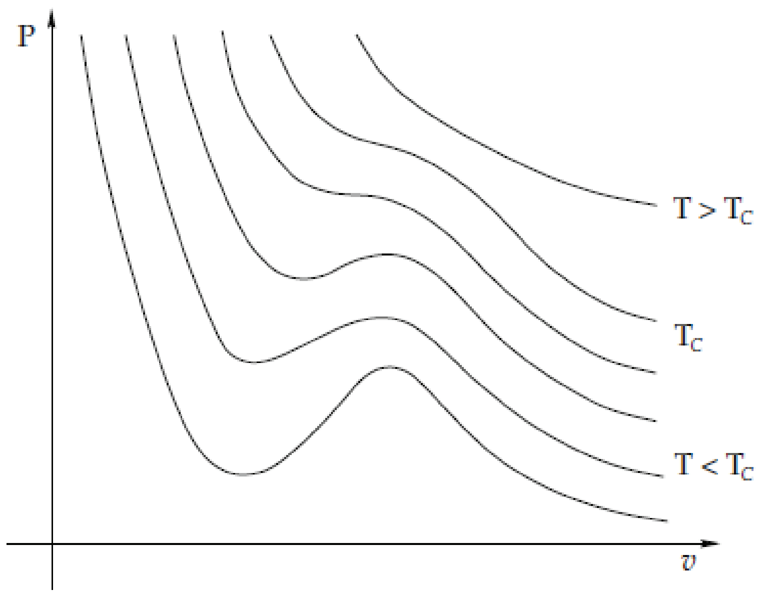
(v specific volume $v = V/N$, V volume, N number of molecules, k Boltzmann constant)

van der Waals passes to $(\mathrm{P} + \frac{a}{v^2})(v - b) = k\mathrm{T}$, as eq. of state for a mole of a real gas

where a/v^2 has to do with inter-molecular attraction and b with the intrinsic volume

($V - bN$ available volume; $a, b > 0$)

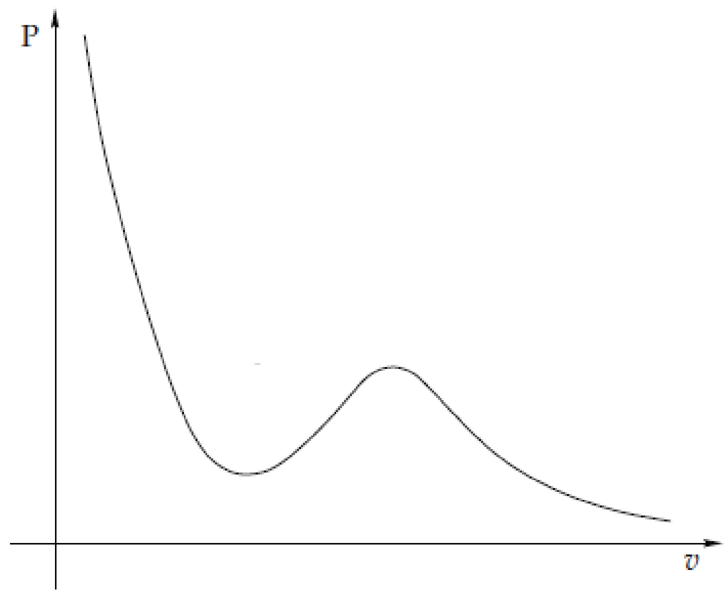
van der Waals isotherms



$$\mathrm{T}_c = 8a/27kb$$

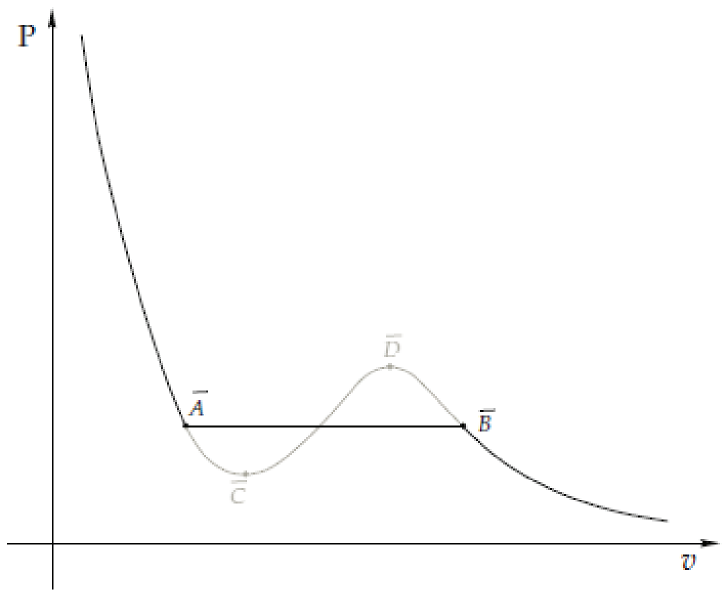
$$\left\{(\mathrm{P}, v)\colon (\mathrm{P} + \frac{a}{v^2})(v - b) = k\mathrm{T}\right\}$$

van der Waals isotherms



Problematic for $\mathrm{T} < \mathrm{T}_c$

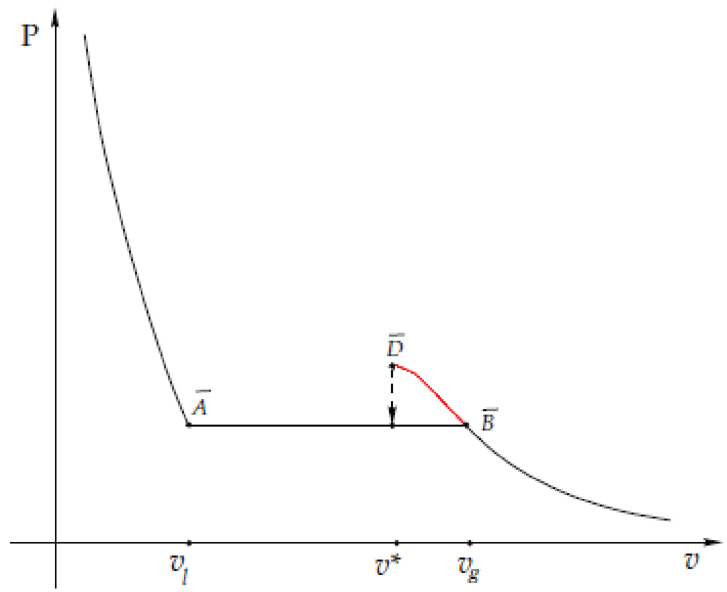
van der Waals isotherms



equal areas Maxwell rule

Maxwell correction: partially justified by thermodynamics

Inhomogeneous system // phase coexistence (vapour/liquid) van der Waals interpretation for "metastable branch"



what about the branches?

van der Waals-Maxwell theory: semi-phenomenological, mean field type analysis

The thermodynamical context gives a very partial justification.

Two problems:

(a) **A more rigorous justification was needed.**

(b) **Treated it as a problem in equilibrium** (**which it is not!**)

Two problems:

(a) **A more rigorous justification was needed.**

• Kac potentials. Lebowitz-Penrose limit (1966) put van der Waals-Maxwell into a statistical mechanics context. (We don't discuss this today)

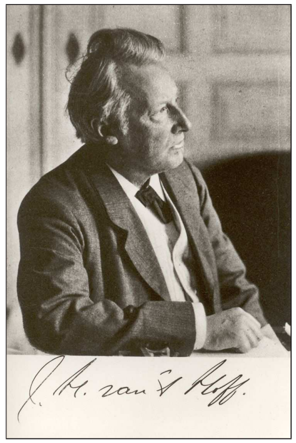
• Analytical continuation (branch) as peculiarity of mean field limit (Isakov (1987), Friedli, Pfister (2004)). (We don't discuss this today)

(b) **Treated it as a problem in equilibrium** (**which it is not**).

• Maxwell already comments on the importance of nucleation and dynamical aspects (Becker e Döring (1935)).

Dynamical early results:

- van't Hoff (1884) - Arrhenius (1889) chemical reaction rate theory

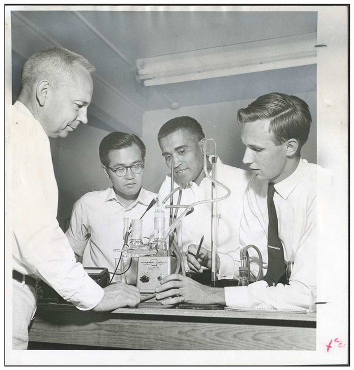


$$R = A \exp\{-E/k\mathrm{T}\} \quad \text{(Arrhenius law)}$$

$1/R$: average reaction time
E: energy
T: temperature

Dynamical early results:

• H. Eyring (1935)   H. A. Kramers (1940) - First derivation of Arrhenius law:

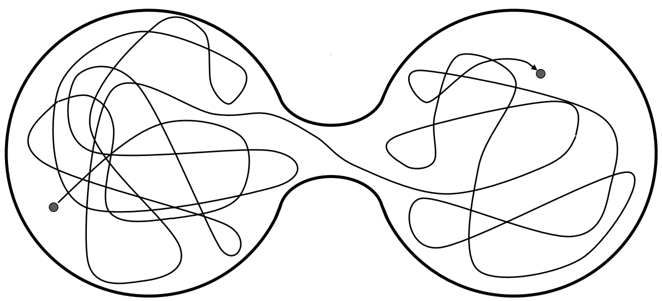


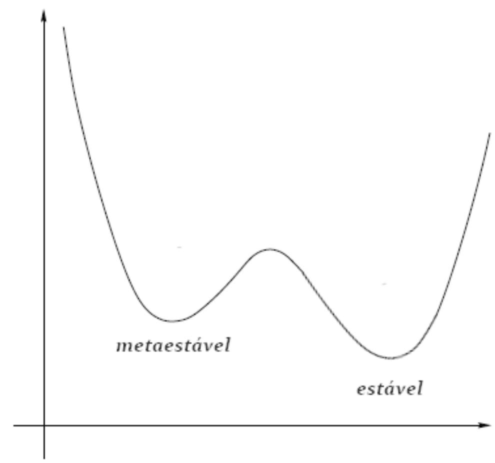
A simple (mesoscopic) model for reaction-diffusion in a regime of large viscosity: $d = 1$,

$$dX(t) = -U'\big(X(t)\big)\,dt + \epsilon\,dB(t),$$

with ϵ a small positive parameter and $U(\cdot)$ a double-well potential (minima at a and b, local maximum at c), $B(\cdot)$ a Brownian motion.

Simple Paradigma:





τ_ϵ time needed to overcome the potential barrier. Kramers gives the prefactor K.

$$E\tau_\epsilon \sim K \exp(\frac{2(U(c) - U(a))}{\epsilon^2})$$ Eyring-Kramers formula

($X(0)$ near a)

Important developments ($d \geq 2$, more general noises, SPDEs): Freidlin-Wentzell theory. Faris, Jona Lasinio (1982)

Potential theoretical tools $\Rightarrow$ good control of prefactors. Eckhoff (2000), Bovier, Eckhoff, Gayrard, Klein (2001)

Evolution of “ensembles”. Lebowitz and Penrose (1970) - From micro to macro

Rigorous proposal to describe Metastability from a statistical mechanical point of view, taking the dynamics into consideration.

Time evolution with an equilibrium measure μ (Gibbs measure) on some space $\mathcal{X}$.

Describe metastable states through certain conditioned measures $\mu_{\mathcal{R}} = \mu(\cdot|\mathcal{R})$. Choice for $\mathcal{R} \subset \mathcal{X}$ driven by three characteristics:

(i) *Only one thermodynamic phase is present.*
(ii) *The lifetime is large, i.e. it takes a long time to exit from* $\mathcal{R}$.
(iii) *Once it escaped from* $\mathcal{R}$, *the return time is much longer.*

- L.-P. applied this to discuss vapour-liquid transition in the case of Kac potentials.

- Cappoccacia, Cassandro, Olivieri (1974) extended to the stochastic Ising model.

Basic message: Equilibrium measures restricted to certain “small” subsets of the phase space; “restricted ensembles” (bottleneck effect).

General remarks about this type of approach:

- Condition (ii) (large lifetime) refers to average behavior;
average lifetime under the measure μ.

  Expressed through very small value of the escape rate $\lambda = \frac{dp_t}{dt}|_{t=0}$, where p_t is the probability of having escaped from $\mathcal{R}$ by time t, if starting from μ_R.

- Time reversibility (usually) plays important role in the verification of (ii).

- Condition (iii) obtained through $\mu(\mathcal{R})$ small.

- Other natural candidates: suitable quasi-stationary measures, conditional ergodicity...
[Miclo (2010), Bianchi, Gaudillière (2016)]

Looking at metastability from a purely dynamical point of view.

It involves two different time scales:

- **Thermalization.** Time to reach the "metastable state"
- **Lifetime of the "metastable state".** Convergence to equilibrium (or stable state)

Mathematical interest:

- Formulation of stochastic models,
- Description of the macroscopic behavior.
- Time scales.

Pathwise approach.

Let $(X_n(t))_{t\geq 0}$ be a family of Markov processes in some space $\mathcal{X}$.

- Two distinct probability measures in $\mathcal{X}$: $\mu_{\mathrm{meta}}, \mu_{\mathrm{eq}}$.
- Time scales θ_n, γ_n with $\theta_n/\gamma_n \to 0$ so that the empirical process

$$\eta_n(t) = \frac{1}{\theta_n} \int_t^{t+\theta_n} \delta_{X_n(s)} ds$$

verifies, as $n \to \infty$:

$$P\Big(\eta_n(t) \approx \mu_{\mathrm{meta}} \quad \text{for all } t < \tau_n - \theta_n\Big) \to 1,$$
$$P\Big(\eta_n(t) \approx \mu_{\mathrm{eq}} \quad \text{for all } t > \tau_n\Big) \to 1,$$

$$P\left(\tau_n/\gamma_n > t\right) \to e^{-t} \quad \text{for all } t.$$

θ_n: upper bound for the time needed to thermalize around the metastable state.

Cassandro, Galves, Olivieri, V. (1984)

- These or similar ideas have then been developed by several authors, in several directions.

Toy examples:

Easy to make some toy examples. They behave essentially as the one dimensional diffusion driven by a double well potential under small noise.

• Birth and death chains

• The so-called Curie-Weiss stochastic chains.

Examples:

• A large class of finite and infinite dimensional diffusions with small noise. (Freidlin-Wentzell regime)

• Supercritical contact process restricted to a finite subgraph (for a large class of graphs)

Interesting relation between cut-off (abrupt convergence to equilibrium) and metastable behavior.

Let us focus on the Ising model $\Rightarrow$

Ising Model (Taking $d = 2$ since the beginning for simplicity)

$\Omega = \{-1, +1\}^{\mathbb{Z}^2}$; $\eta \in \Omega$; $\Lambda \subset \mathbb{Z}^2$ finite; $\Omega_\Lambda = \{-1, +1\}^\Lambda$.

For $\sigma \in \Omega_\Lambda$:

$$H_{\Lambda,\eta,h}(\sigma) = -\sum_{\substack{\{x,y\}\subset\Lambda \\ |x-y|=1}} \sigma(x)\sigma(y) - \frac{h}{2}\sum_{x\in\Lambda}\sigma(x) - \sum_{\substack{x\in\Lambda, y\notin\Lambda \\ |x-y|=1}} \sigma(x)\eta(y)$$

and the probability measure on Ω_Λ

$$\mu_{\Lambda,\eta,h}(\sigma) = \frac{e^{-\beta H_{\Lambda,\eta,h}(\sigma)}}{Z_{\Lambda,\eta,h}}$$

where $Z_{\Lambda,\eta,h}$ is the normalizing constant (partition function).

$1/\beta$ represents the temperature ($\beta = \frac{1}{kT}$ as before)

Basic interest: It combines simplicity with a rich structure in the limit $\Lambda \to \mathbb{Z}^2$ (also called thermodynamic limit).

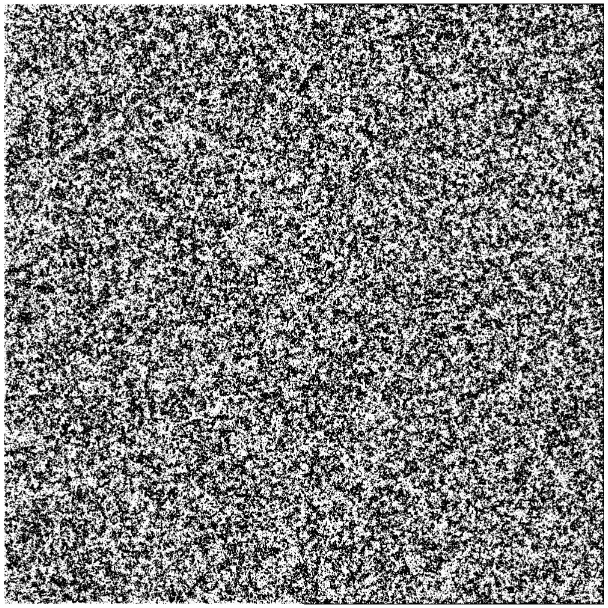
Lenz (1920); Ising (1925) $d = 1$; Peierls (1936), Onsager (1944) $d = 2$, Yang and Lee (1952)...

It exhibits **phase transition**:

- There exists $\beta_c \in (0, \infty)$ so that for $h = 0$ there are multiple limiting measures when $\beta > \beta_c$:
  $\eta(\cdot) \equiv -1$ brings to $\mu_{\beta,-} \neq \mu_{\beta,+}$ obtained when $\eta(\cdot) \equiv +1$.
- It is a first order phase transition. The phenomenon of spontaneous magnetization occurs:

$$\lim_{h \to 0+} \mu_{\beta,h}(\sigma(0)) = \mu_{\beta,+}(\sigma(0)) = m^*_\beta > 0$$

high temperature (β small) – disorder   Simulations by Vincent Beffara



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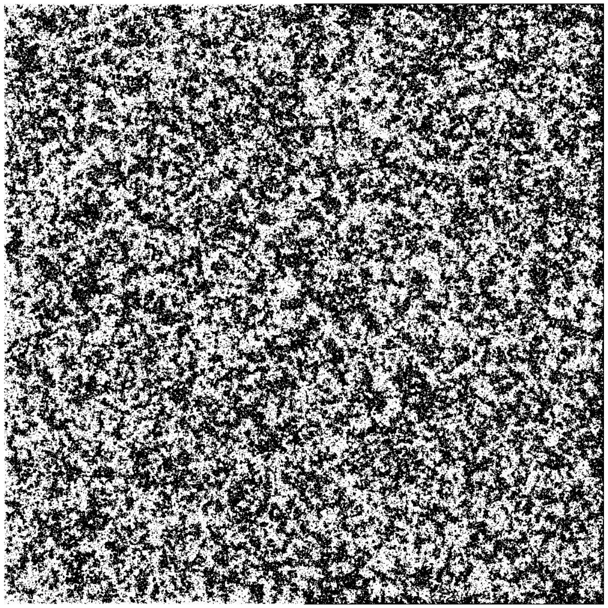

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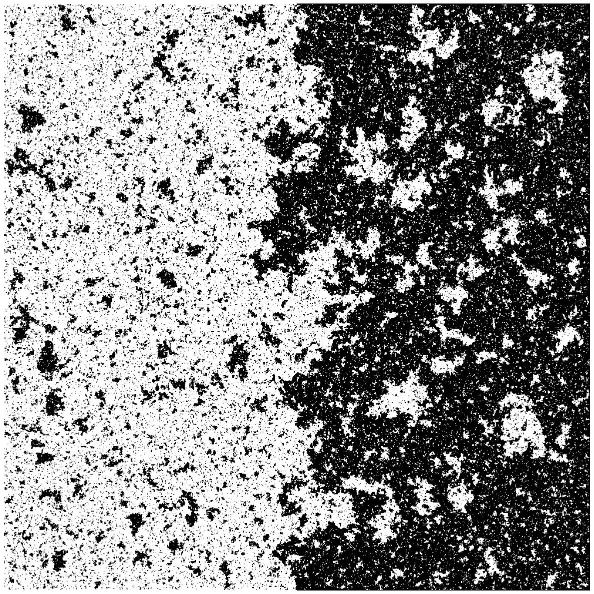
near criticality $\beta \approx \beta_c$ Simulations by Vincent Beffara



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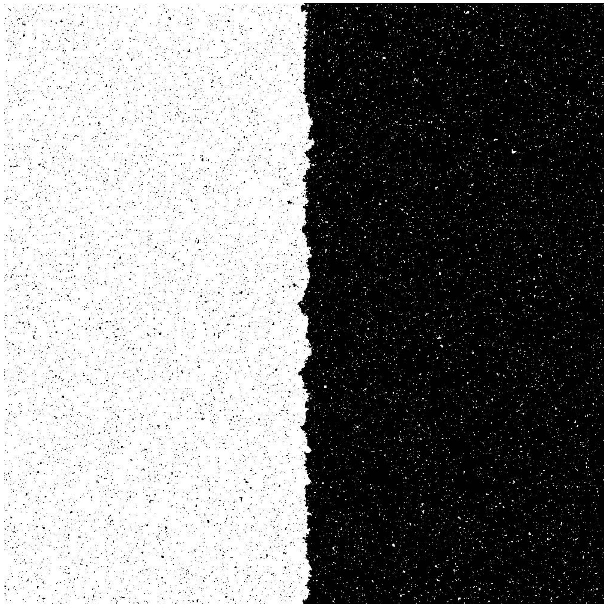
low temperature (β large) – long-range order Simulations by Vincent Beffara



Our plan: To discuss metastability for fixed $\beta > \beta_c$ and $h \downarrow 0$ (as in the hysteresis loop) through an stochastic dynamics.

Continuous time Markov processes on Ω_Λ: $X_{\Lambda,\eta,h} = \big(X_{\Lambda,\eta,h}(t)\big)_{t\geq 0}$

with a single spin flip generator

$$(\mathcal{L}_{\Lambda,\eta,h} f)(\sigma) = \sum_{x\in\Lambda} c(\sigma,\sigma^x)\left(f(\sigma^x) - f(\sigma)\right), \qquad f:\Omega_\Lambda \to \mathbb{R}, \qquad \sigma \in \Omega_\Lambda,$$

where

$$\sigma^x(y) = \begin{cases} \sigma(y) & \text{if } x \neq y, \\ -\sigma(x) & \text{if } x = y, \end{cases}$$

and the flip rates $c(\sigma,\sigma^x)$ satisfy the reversibility condition

$$\mu_{\Lambda,\eta,h}(\sigma)c(\sigma,\sigma^x) = \mu_{\Lambda,\eta,h}(\sigma^x)c(\sigma^x,\sigma), \qquad \sigma \in \Omega_\Lambda, \qquad x \in \Lambda.$$

Example: Metropolis dynamics with

$$c(\sigma,\sigma^x) = \exp\left\{-\beta\big(H_{\Lambda,\eta,h}(\sigma^x) - H_{\Lambda,\eta,h}(\sigma)\big)^+\right\}, \qquad \sigma \in \Omega_\Lambda, \qquad x \in \Lambda,$$

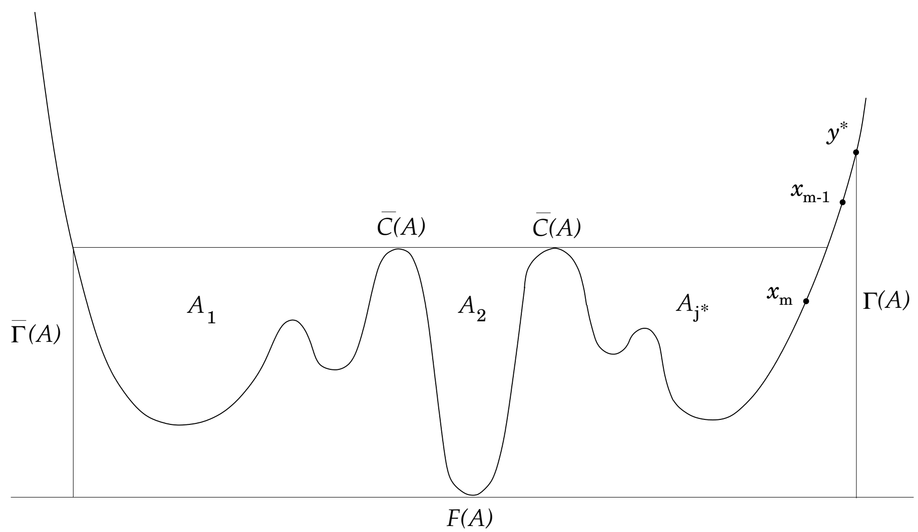
where $(a)^+ = \max\{a, 0\}$,

Stochastic Ising models: Many results in the regime $\beta \to \infty$ (Vanishing temperature)

Neves, Schonmann (1991); Catoni, Cerf (1995), Scoppola (1995), Olivieri, Scoppola (1995), den Hollander et al (2000), Bovier, Manzo (2001); Ben Arous, Cerf (2001), Manzo, Olivieri (2001), Larralde, Leyvraz, Sanders (2007), ...

Markov chains in the Freidlin-Wentzell regime: $p^{(\beta)}(i,j) \approx e^{-\beta \Delta_{i,j}}: i,j \in \mathcal{X}$
(Λ fixed, finite)

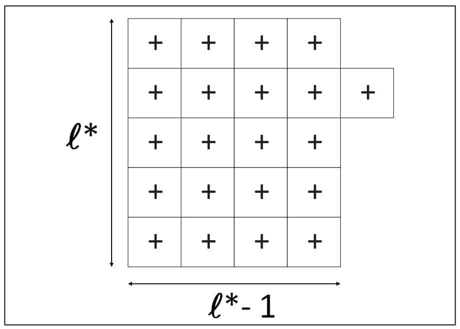
Main tools: large deviations, renormalization, potential theoretical tools.
Understanding the energy landscape, identifying critical droplets (or critical configurations):

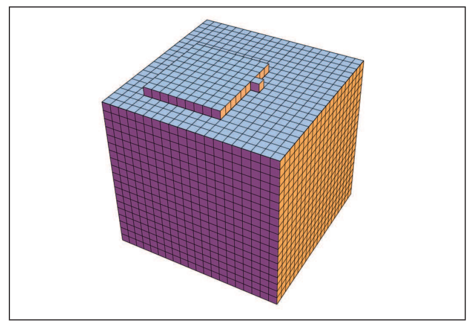


Stochastic Ising models: Many results in the regime $\beta \to \infty$ (Vanishing temperature)

Simplest situation: Finite volume Λ, fixed (suitably small) magnetic field $h > 0$, $\beta \to \infty$:

Neves, Schonmann ($d = 2$); Ben Arous, Cerf ($d = 3$) - **pathwise approach applied**





critical droplets when $d = 2$ and $d = 3$

Notice: this is not in the regime of the hysteresis loop.

Simulation $\Rightarrow$

Schonmann and Shlosman (1998): studied infinite volume dynamics for $\beta > \beta_c$, $h \downarrow 0$.

Initial measure $\nu \preceq \mu_-$, considered times $t = e^{\alpha/h}$. $(\mu_- = \mu_{\beta,-})$

Identify critical α_c: f any local observable

- If $\alpha < \alpha_c$, $\mathbb{E}_\nu[f(X_\infty(t))] = \sum_{j<k} \frac{h^j}{j!} \frac{d^j \mu_h(f)}{dh^j}\Big|_{h=0_-} + O(h^k)$ (for any k)$\approx \mu_-(f)$

- If $\alpha > \alpha_c$, $\mathbb{E}_\nu[f(X_\infty(t))] \approx \mu_h(f) \quad \approx \mu_+(f)$

Proved the remarkable formula:

$$\alpha_c = \frac{\beta w_\beta^2}{12 m_\beta^*} \text{ an equilibrium quantity!}$$

with w_β is the integrated surface tension of the unitary area Wulff shape W.

Main tools: Large deviations and Wulff shape construction.
Pfister (1991); Dobrushin, Kotecky, Shlosman (1992); Ioffe (1995)

Two drops about the Wulff shape

• Surface tension $\tau(\vartheta)$: free energy per unit length of an interface between the $+$ and $-$ phases in the direction orthogonal to $(\cos\vartheta, \sin\vartheta)$.

• Wulff functional of a rectifiable curve $\gamma \subset \mathbb{R}^2$, $\gamma = \partial D$ $D \subset \mathbb{R}^2$ simply connected domain:

$$\mathcal{W}(\gamma) = \oint_\gamma \tau(\theta_s)\, ds, \qquad (\vartheta_s \text{ direction of the external normal })$$

• Wulff shape: its boundary minimizes $\mathcal{W}$ among all the rectifiable boundaries of domains with a given volume.

It is defined for $\rho > 0$ and up to dilatation and translation by

$$W_\rho = \bigcap_{\vartheta \in [0,2\pi]} \left\{ x = (u,v) \in \mathbb{R}^2 : u\cos\vartheta + v\sin\vartheta \le \rho\tau(\vartheta) \right\}.$$

W: when ρ is such that area$(W) = 1$.

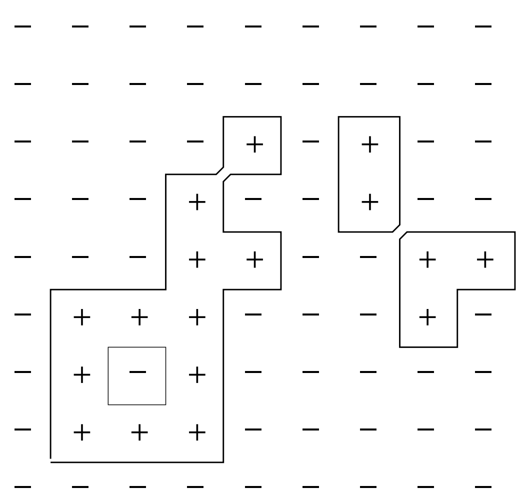
Gaudillière, Milanesi, V. - pathwise description of the transition

Dynamics $X_{\Lambda_h,-,h}$ on a suitable domain Λ_h with area $(B_{\max}/h)^2$ for $B_{\max}$ large enough:

Configurations fixed to $\eta(x) = -1, \forall x \notin \Lambda_h$. $h > 0, h \downarrow 0$

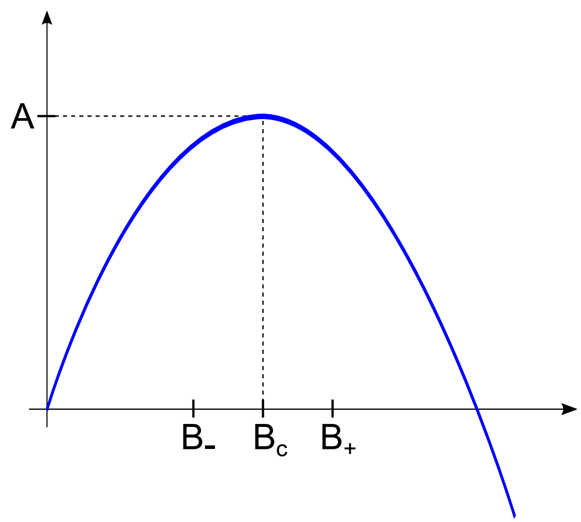
- μ_- represents the metastable state;
- $\mu_{\beta,h} \approx \mu_+$ represents the stable state.

Configurations described through self-avoiding contours on the dual lattice.



Simple heuristics: Free energy of a "plus phase" Wulff droplet of area $(B/h)^2$ in a "minus phase" (metastable) is estimated by: (for $h \ll 1$ and up to an additive constant)

$$w_\beta \frac{B}{h} - 2m_\beta^* \frac{h}{2}\left(\frac{B}{h}\right)^2 = \frac{1}{h}\left(w_\beta B - m_\beta^* B^2\right) = \frac{1}{h}\phi(B)$$



$A = \frac{w_\beta^2}{4m_\beta^*}$ max value of ϕ, attained at $B_c = \frac{w_\beta}{2m_\beta^*}$.

• In a sufficiently large volume: droplets with area $(B/h)^2$ with $B < B_c$ ($B > B_c$) tend to shrink (grow) due to $h > 0$.

Mixing time:

$$t_{\text{mix},h} = \inf\left\{t \geq 0 : \forall\sigma,\ \forall F,\ \left|\mathbb{P}_\sigma\left(X_{\Lambda_h,-,h}(t) \in F\right) - \mu_{\Lambda_h,-,h}(F)\right| \leq \frac{1}{e}\right\},$$

Proposition For any $\beta > \beta_c$, $B_{\max} > 2B_c$

$$\lim_{h\to 0} h \ln(t_{\text{mix},h}) = \beta A$$

Notice!

$$\alpha_c = \frac{\beta A}{3}$$

Theorem (Gaudillière, Milanesi, V.)

For all $\beta > \beta_c$, $B_{\max} > 2B_c$, can choose B_+ so that for the process starting with ν, any observable f, $\exists \delta > 0, h_0 > 0$ so that:

(i) If $\nu = \mu_{\Lambda_h,-,h}(\cdot\,|\mathcal{R})$, $\exists$ random time T_h so that:

- $T_h/t_{\mathrm{mix},h}$ converges in law to an exponential r.v. of mean 1
- $\lim_{h\to 0} \mathbb{P}_\nu \left(\theta < T_h, \sup_{t<T_h-\theta} \left| A_\theta(t,f) - \mu_{\Lambda_h,-,h}\big(f|\mathcal{R}\big)\right| \le \|f\|_\infty e^{-\delta/h} \right) = 1,$

where

$$A_\theta(t,f) = \frac{1}{\theta}\int_t^{t+\theta} f(X_{\Lambda_h,-\underline{1},h}(u))du$$

with

$$\theta \approx \exp\left\{ \frac{1}{2}\left(\frac{\beta A}{h}\right)\right\}.$$

(ii) For all $h < h_0$, and any starting measure ν:

$$|\mathbb{E}_\nu\left[f\left(X_{\Lambda_h,-,h}(T_h)\right)\right] - \mu_{\Lambda_h,-,h}(f)| \le \|f\|_\infty e^{-\delta/h}.$$

What is $\mathcal{R}$? How is T_h defined?

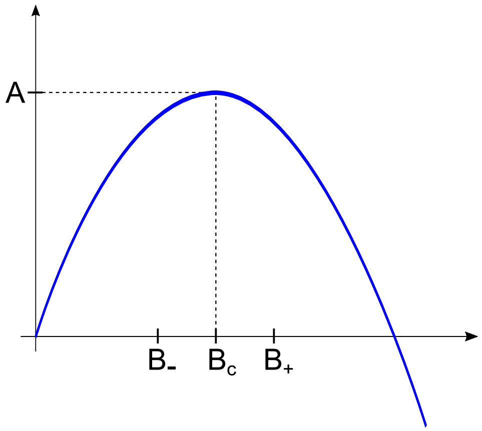
• We use the sets:

• $\mathcal{R}$: all contours which are not truly small can be included in a certain number ($<< 1/h$) of disjoint Wulff shapes total length is at most B_+/h.

• Good interpolation between $\mu(\cdot|\mathcal{R})$ and the quasi stationary measure.

As for T_h we allow some excursions in $\mathcal{S} \setminus \mathcal{R}$, where

• $\mathcal{S}$: the configurations for which there exist an external contour enclosing a Wulff shape of area $(B_-/h)^2$.



- More precisely:

  T_h is the killing time if while in $\mathcal{S}$ the process is killed with rate λ.

Main technical point for the proof of the theorem:

The relaxation time of the process restricted to $\mathcal{R}$ is much smaller than T_h.

References:

• Gaudillière, A. ; Milanesi, P. ; Vares, M. E. *Asymptotic Exponential Law for the Transition Time to Equilibrium of the Metastable Kinetic Ising Model with Vanishing Magnetic Field.* Jr. Stat. Phys. 179, 263 - 308, 2020. https://doi.org/10.1007/s10955-019-02463-5
(many references can be found in this paper)

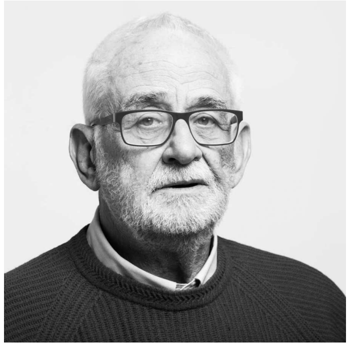
Two monographs on the subject:

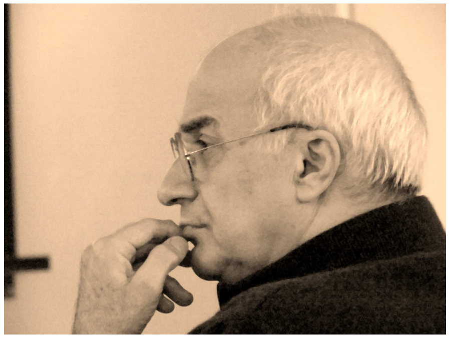
• Bovier, A; den Hollander, F. Metastability. A Potential-Theoretic Approach. (Springer, 2015)

• Olivieri, E.; Vares, M.E. Large Deviations and Metastability. (Cambridge University Press, 2004)

Em Marseille com Alex Gaudillière e Paolo Milanesi

Co-authors pathwise approach: Marzio Cassandro, Antonio Galves, Enzo Olivieri





Obrigada!