

Metastability for continuum interacting particle systems

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Problem

Question:

How long does it take to go from *gas* to *condensed* phase? Typically, if the density is only slightly smaller than *saturation density*: it takes a long time – there is a **nucleation barrier** to overcome.

Physics / thermodynamics: topic of **nucleation theory**.

This talk:

stochastic approaches to **metastability** for Markovian dynamics whose stationary measures are Gibbs measures. Adapt existing results for **lattice spin systems to continuum**. BIANCHI, BOVIER, ECKHOFF, DEN HOLLANDER, GAYRARD, IOFFE, KLEIN, MANZI, NARDI, SLOWIK, SPITONI...

Limitations:

We *do not know* whether the system actually has a gas / condensed phase transition at positive temperature. But: this does not bother us because we work in the **zero-temperature limit** at **fixed finite volume**.

Moreover, *artificial dynamics* – particles appear and disappear out of the blue. Expected: methods carry over to a whole class of Markovian dynamics.

Outline

1. Model
2. Main result (proof in progress)
3. Key proof ingredient: potential-theoretic approach
4. Application to our problem

Grand-canonical Gibbs measure

- ▶ $L > 0$, box $\Lambda = [0, L] \times [0, L]$.
- ▶ $\beta > 0$ inverse temperature, $\mu \in \mathbb{R}$ chemical potential
- ▶ $v : [0, \infty) \rightarrow \mathbb{R} \cup \{\infty\}$ pair potential – *soft disk potential* RADIN '81

$$v(r) = \begin{cases} \infty, & r < 1 \\ 24r - 25, & 1 \leq r \leq 25/24, \\ 0, & r > 25/24. \end{cases}$$

- ▶ Total energy $U(\{x_1, \dots, x_n\}) := \sum_{i < j} v(|x_i - x_j|)$, $U(\emptyset) = U(\{x\}) = 0$.
- ▶ Probability space:

$$\Omega := \{\omega \subset \Lambda \mid \text{card}(\omega) < \infty\}.$$

Reference measure: Poisson point process Q , intensity parameter 1.

Grand-canonical Gibbs measure $P = P_{\beta, \mu, \Lambda}$

$$\frac{dP}{dQ}(\omega) = \frac{1}{\Xi} \exp\left(-\beta(U(\omega) - \mu n(\omega))\right),$$

$n(\omega) := \text{card}(\omega)$ = number of points in configuration ω .

$\Xi = \Xi_{\Lambda}(\beta, \mu)$ grand-canonical partition function.

Dynamics

Combine interaction energy and chemical potential

$$H(\omega) := U(\omega) - \mu n(\omega).$$

Dynamics: **Metropolis**-type **Markov process** with generator

$$(Lf)(\omega) := \sum_{x \in \omega} \exp(-\beta[H(\omega \setminus x) - H(\omega)]_+) (f(\omega \setminus x) - f(\omega)) \\ + \int_{\Lambda} \exp(-\beta[H(\omega \cup x) - H(\omega)]_+) (f(\omega \cup x) - f(\omega)) dx.$$

Birth and death process: particles appear and disappear anywhere in the box. Rates are exponentially small in β if adding / removing particle increases $H(\omega)$. Grand-canonical **Gibbs measure is reversible**.

Analogue of spin-flip dynamics for lattice spin systems: **Glauber dynamics**. Used in numerical simulations under the name **grand-canonical Monte-Carlo**. Studied in finite and infinite volume GLÖTZL '81; BERTINI, CANCRINI, CESI '02; KUNA, KONDRATIEV, RÖCKNER ...

Warm-up for more "realistic" dynamics (particles hop / diffuse).

Metastable regime

We are interested in the limit $\beta \rightarrow \infty$ at fixed μ , fixed Λ .

The equilibrium measure $P_{\beta, \mu, \Lambda}$ will concentrate on minimizers of $H(\omega) = U(\omega) - \mu n(\omega)$. Observe

$$\min_{\omega} H(\omega) = \min_{k \in \mathbb{N}_0} \min_{n(\omega)=k} (U(\omega) - \mu n(\omega)) = \min_{k \in \mathbb{N}_0} (E_k - k\mu).$$

Ground states:

$$E_k := \min_{n(\omega)=k} U(\omega) = -3k + \lceil \sqrt{12k - 3} \rceil.$$

Every minimizer of U is a subset of a **triangular lattice** of spacing 1.

Three cases:

1. $\mu < -3$: $k \mapsto E_k - k\mu$ increasing, minimizer $k = 0$.
Minimum = empty box.
2. $\mu > -2$: $k \mapsto E_k - k\mu$ decreasing, minimizer: k large.
Minimum = filled box.
3. $-3 < \mu < -2$: local minimum at $k = 0$, global minimum: k large.
Empty box = metastable, filled box = stable. **Metastable regime.**

Question: for $\mu \in (-3, -2)$, how long does it take to go from empty to full?

Critical and protocritical droplets

Write $\mu = -3 + h$.

Assumption $\mu \in (-3, 2)$ ($h \in (0, 1)$) and $h^{-1} \notin \frac{1}{2}\mathbb{N}$.

Set

$$\ell_c := \left\lfloor \frac{1}{h} \right\rfloor.$$

Proposition The map $k \mapsto E_k - k\mu$ has a unique maximizer k_c ,

$$k_c = \begin{cases} (3\ell_c^2 + 3\ell_c + 1) - (\ell_c + 1) + 1, & h \in (\frac{1}{\ell_c+1/2}, \frac{1}{\ell_c}), \\ (3\ell_c^2 + 3\ell_c + 1) + \ell_c + 1, & h \in (\frac{1}{\ell_c+1}, \frac{1}{\ell_c+1/2}). \end{cases}$$

Note: $3\ell_c^2 + 3\ell_c + 1 =$ no. of particles in equilateral hexagon of sidelength ℓ_c .

Proposition Let $k_p := k_c - 1$. The minimizer of $U(\omega)$ with $n(\omega) = k_p$ is unique, up to translations and rotations – obtained from an equilateral hexagon of sidelength ℓ_c by adding or removing one row. **Protocritical droplet**. **Critical droplet** = protocritical droplet + a protuberance.

Proof: builds on RADIN '81. Related: AU YEUNG, FRIESECKE, SCHMIDT '12.

Generalization of known results for Ising / square lattice to triangular lattice + continuum degrees of freedom.

Target theorem

Time to reach dense configurations:

$$D = \{\omega \in \Omega \mid n(\omega) \geq \rho_0 |\Lambda|\},$$
$$\tau_D := \inf\{t > 0 \mid \omega_t \in D\}.$$

$\rho_0 \approx$ density of the triangular lattice.

Goal: as $\beta \rightarrow \infty$,

$$\mathbb{E}_\emptyset \tau_D = (1 + o(1)) C(\beta)^{-1} \exp(\beta \Gamma)$$

Energy barrier:

$$\Gamma = \max_{k \in \mathbb{N}} (E_k - k\mu) = E_{k_c} - k_c \mu.$$

Prefactor:

$$C(\beta) \approx 2\pi |\Lambda| \times \frac{1}{(24\beta)^{2k_c-3}} \times \text{a finite sum over critical droplet shapes.}$$

Generalizes results for Glauber dynamics on square lattice. Principal difference: prefactor β -dependent. Appearance of derivative $v'(1+) = 24$ reminiscent of Eyring-Kramers formula (transition times for diffusions). **Blends discrete and continuous** aspects.

Details & interpretation

Inverse of the hitting time: intermediate expression

$$(\mathbb{E}_{\emptyset} \tau_D)^{-1} \sim \frac{1}{\equiv} \int_{\{n(\omega)=k_c\}} \frac{|L(\omega)|}{1 + |L(\omega)|} \exp(-\beta H(\omega)) Q(d\omega).$$

with

$$L(\omega) = \{y \in \Lambda \mid H(\omega \cup y) \leq H(\omega) \text{ and } (*)\} \subset \Lambda$$

(*) there is a sequence $\omega_k = \omega \cup \{y, y_1, \dots, y_k\}$ $k = 1, \dots, n$ such that $H(\omega_k) < \Gamma$ for all k and $\omega_n \in D$.

Evaluation:

- ▶ As $\beta \rightarrow \infty$, **only a small neighborhood of critical droplets** (quasi-hexagon + protuberance) **contributes** to the integral.
- ▶ $|L(\omega)|/(1 + |L(\omega)|)$ = **probability that a critical droplet ω grows rather than shrinks.**
- ▶ **probability of seeing a critical droplet:** $2\pi|\Lambda|$ (position in space + orientation) \times a Laplace type integral over droplet-internal degrees of freedom.
- ▶ Evaluation as $\beta \rightarrow \infty$ gives leads to powers of β , **sum over possible shapes of critical droplets** (location of the protuberance).

Potential theoretic approach

(X_t) irreducible Markov process with finite state space V , transition rates $q(x, y)$, ($x \neq y$). Reversible measure $m(x)$. Conductance:

$$c(x, y) = m(x)q(x, y) = m(y)q(y, x).$$

A, B disjoint sets, $A = \{a\}$ singleton. Representation of the hitting time:

$$\mathbb{E}_a \tau_B = \frac{1}{\text{cap}(a, B)} \sum_{x \in V} h(x) m(x)$$

$h(x) = \mathbb{P}_x(\tau_a < \tau_B)$ unique solution of the Dirichlet problem

$$h(a) = 1, \quad h(b) = 0 \quad (b \in B),$$

$$(Lh)(x) = \sum_{y \in V, y \neq x} q(x, y)(h(y) - h(x)) = 0 \quad (x \in V \setminus (\{a\} \cup B)).$$

"Capacity" or effective conductance:

$$\text{cap}(a, B) = \sum_{y \in V} q(a, y)(h(a) - h(y)) = (-Lh)(a).$$

Well-known formulas. Have analogues for continuous state spaces.

Potential theoretic approach, continued

Dirichlet form and Dirichlet principle:

$$\mathcal{E}(f) = \frac{1}{2} \sum_{x,y \in V} c(x,y) (f(y) - f(x))^2$$

$$\text{cap}(A, B) = \min \{ \mathcal{E}(f) \mid f|_A = 1, f|_B = 0 \}.$$

Instead of computing hitting times, we have to estimate capacities. Facilitated by variational principles: Dirichlet, Thomson, Berman-Konsowa.

Remark: vocabulary (capacity / conductance) hybrid of two distinct pictures:

- ▶ Random walks \leftrightarrow electric networks: network of resistors, $c(x,y) = 1/r(x,y) =$ conductance, $f(x) =$ voltage at node x , $\mathcal{E}(f) =$ power of dissipated energy. Think

$$\mathcal{P} = UI = RI^2 = CU^2.$$

- ▶ Probabilistic potential theory (Brownian motion \leftrightarrow Laplacian): Dirichlet form = electrostatic energy, think

$$\mathcal{E}(\varphi) = \frac{1}{2} \int \varepsilon(x) |\nabla \varphi(x)|^2 dx.$$

Application to continuum Glauber dynamics

Dirichlet form:

$$\begin{aligned}\mathcal{E}(f) &= \frac{1}{2} \int_{\Omega} f(x)(-Lf)(x) P_{\beta, \mu, \Lambda}(d\omega) \\ &= \frac{1}{2} \int_{\Omega} \int_{\Lambda} e^{-\beta \max(H(\omega), H(\omega \cup x))} (f(\omega \cup x) - f(\omega))^2 dx Q(d\omega)\end{aligned}$$

Network with edges $(\omega, \omega \cup x)$, conductances $\exp(-\beta \max[H(\omega), H(\omega \cup x)])$.

More precisely: **conductance** is a **measure** $K(d\omega, d\tilde{\omega})$ on $\Omega \times \Omega$,

$$\mathcal{E}(f) = \frac{1}{2} \int_{\Omega \times \Omega} (f(\omega) - f(\tilde{\omega}))^2 K(d\omega, d\tilde{\omega}).$$

Wanted: effective conductance (capacity) between $A = \{\emptyset\}$ and $B = D =$ dense configurations as $\beta \rightarrow \infty$.

Upper bound with Dirichlet principle – $\text{cap}(\emptyset, D) \leq \mathcal{E}(f)$, $f =$ guessed good test function.

Lower bound with Berman-Konsowa principle: capacity as a *maximum* over probability measures on paths from \emptyset to D .

Finite state space: BERMAN, KONSOWA '90.

Reversible jump processes in Polish state spaces DEN HOLLANDER, J. '13.

Berman-Konsowa principle and state of the proof

Berman-Konsowa principle:

- ▶ \mathbb{P} probability measure on paths $\gamma = (\omega_0, \dots, \omega_n)$ from \emptyset to D
- ▶ $\Phi_{\mathbb{P}}$ flow: $\Phi_{\mathbb{P}}(C_1 \times C_2) =$ expected no. of edges from C_1 to C_2 (*measure*).
- ▶ Variational representation for the capacity:

$$\text{cap}(\emptyset, D) = \sup_{\mathbb{P}} \mathbb{E} \left[\left(\sum_{(x,y) \in \gamma} \frac{d\Phi_{\mathbb{P}}}{dK}(x,y) \right)^{-1} \right].$$

- ▶ Lower bound for the capacity: guess a test measure \mathbb{P} on paths.

State of the proof for asymptotics of the hitting time:

- ▶ Proof nearly complete for time to become *supercritical*, i.e., modified choice of D

$$\tilde{D} = \{\omega \in \Omega \mid n(\omega) \geq k_c + 1\}.$$

- ▶ For original choice $D = \{n(\omega) \geq \rho_0 |\Lambda|\}$, need to answer an additional question about energy landscape, “no-deep-well property”. **Open**.

If property does not hold, it is possible that the Glauber dynamics gets stuck in configuration in $\tilde{D} \setminus D$.