The Widom-Rowlinson model: metastability, mesoscopic and microscopic fluctuations for the critical droplet

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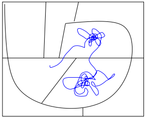
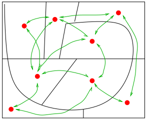
What is metastability?

Metastability is a phenomenon where a system, under the influence of a stochastic dynamics, moves between different regions of its state space on different time scales.





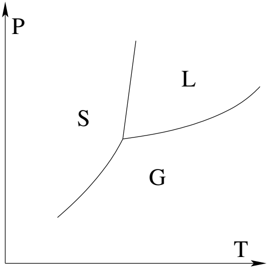
Fast time scale:
quasi-equilibrium within single subregion

Slow time scale:
transitions between different subregions

Monographs:

- Olivieri and Vares 2005
- Bovier and den Hollander 2015

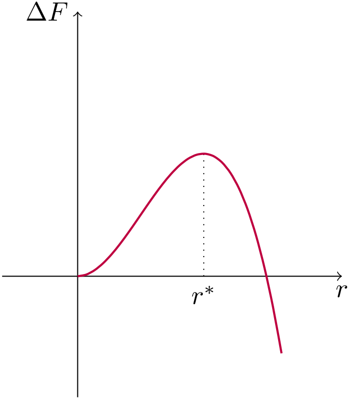
Metastable behaviour is the dynamical manifestation of a first-order phase transition. We focus on condensation.



When vapour is cooled rapidly below the critical temperature, we see that the system will persist for long time in a metastable vapour state (supersaturated gas) before transiting (rapidly) to the new stable liquid state under some random fluctuations.

Why?

Metastable behaviour is the dynamical manifestation of a first-order phase transition. We focus on condensation.



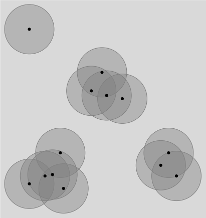
The system has to form a critical droplet of liquid to trigger the crossover, which then will grow and invade the whole space. But many unsuccessful attempts because forming small droplets results in an increasing of free energy...

Models in the continuum

- Several results for metastable behaviour of stochastic models on the lattice
- Continuum systems modelling fluids are very difficult to study. Rigorous proof of the presence of phase transitions has been achieved only for few models:
  - Widom-Rowlinson model (Ruelle, '71)
  - Kac models with 2-body attraction and 4-body repulsion (Lebowitz, Mazel and Presutti, '99)
- Metastability for continuum systems:
  - Crystalisation of 2-dimensional particles interacting via a soft-disk potential (Jansen and den Hollander, in preparation)
  - We will focus on the Widom-Rowlinson model, adapting what has been done in the discrete.

The static Widom-Rowlinson model: Hamiltonian

Let $\mathbb{T} \subset \mathbb{R}^2$ be a finite torus. The set of finite particle configurations in $\mathbb{T}$ is $\Gamma = \{\gamma \subset \mathbb{T} \colon N(\gamma) \in \mathbb{N}_0\}$, $N(\gamma)$: cardinality of γ



- Halo of a configuration

$$h(\gamma) = \bigcup_{x \in \gamma} B_1(x)$$

$$V(\gamma) := |h(\gamma)|$$

- Hamiltonian

$$H(\gamma) = V(\gamma) - N(\gamma)\pi$$

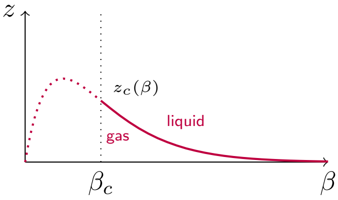
$\Rightarrow \quad -(N(\gamma) - 1)\pi \leq H(\gamma) \leq 0$ (attractive)

The static Widom-Rowlinson model: Gibbs measure

The grand-canonical Gibbs measure is

$$\mu_\beta(\mathrm{d}\gamma) = \frac{z^{N(\gamma)}}{\Xi}\, \mathrm{e}^{-\beta H(\gamma)} \mathbb{Q}(\mathrm{d}\gamma),$$

- $\mathbb{Q}$: Poisson point process with intensity 1
- $z \in (0, \infty)$: activity
- $\beta \in (0, \infty)$: inverse temperature
- Ξ: normalising partition function



Coexistence line:

$$z_c(\beta) = \beta e^{-\pi\beta}$$

$$\beta < \beta_c \qquad \text{single phase}$$

$$\beta > \beta_c \qquad \text{two phases: gas/liquid}$$

Phase transition at the thermodynamic limit, i.e. $\mathbb{T} \to \mathbb{R}^d$.
(D. Ruelle, '71; J.T. Chayes, L. Chayes and R. Kotecký, '95)

The dynamic WR model

Heat bath dynamics

Particle configuration is a continuous-time Markov process $(\gamma_t)_{t\geq 0}$ with state space Γ and with generator

$$(Lf)(\gamma) = \int_{\mathbb{T}} \mathrm{d}x \; b(x,\gamma)\,[f(\gamma \cup x) - f(\gamma)] + \sum_{x\in\gamma} d(x,\gamma)\,[f(\gamma \backslash x) - f(\gamma)]$$

where particles are added at rate b and removed at rate d

$$b(x,\gamma) = z\, e^{-\beta[H(\gamma\cup x) - H(\gamma)]}, \quad x \notin \gamma, \qquad d(x,\gamma) = 1, \quad x \in \gamma.$$

The grand-canonical Gibbs measure is reversible, i.e.

$$b(x,\gamma)\, e^{-\beta H(\gamma)} = d(x, \gamma\cup x)\, e^{-\beta H(\gamma\cup x)}, \qquad x \notin \gamma, \quad \gamma \in \Gamma.$$

Key question of metastability

- Start with **empty box** $\square = \emptyset$ (preparation in vapour state),
- Choose $z = \kappa\, z_c(\beta) = \kappa\, \beta\, \mathrm{e}^{-\beta\pi}$, $\kappa \in (1, \infty)$, (reservoir is supersaturated vapour),
- Wait for the first time the system reaches the **full box** $\blacksquare = \{\gamma \in \Gamma : h(\gamma) = \mathbb{T}\}$ (condensation to liquid state).

Question: In the regime

$$\beta \to \infty$$

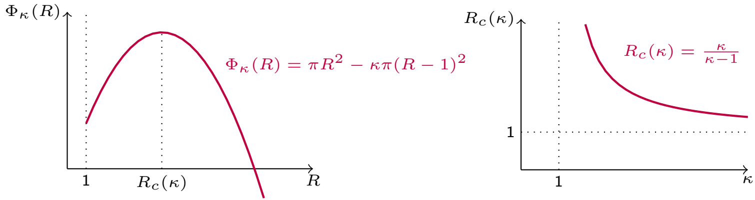
$$\mathbb{T} \quad \text{fixed}$$

find precise asymptotics of the mean hitting time

$$\mathbb{E}_{\square}(\tau_{\blacksquare}), \qquad \text{where} \qquad \tau_{\blacksquare} = \inf\{t > 0\colon\ \gamma_t = \blacksquare\}$$

and describe the shape of the critical droplet.

Main objective: find the mean hitting time



Target Theorem 1 [Arrhenius formula]

For every $\kappa \in (1,\infty)$,

$$\mathbb{E}_{\square}(\tau_{\blacksquare}) = \exp\left[\beta\,\Phi(\kappa) - \beta^{1/3}\Psi(\kappa) + o(\beta^{1/3})\right], \quad \beta \to \infty$$

where

$$\Phi(\kappa) := \Phi_\kappa(R_c(\kappa)) = \frac{\pi\kappa}{\kappa - 1}$$

$$\Psi(\kappa) = s\,\frac{\kappa^{2/3}}{\kappa - 1}$$

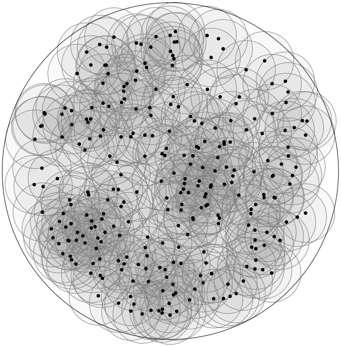
where $s \in \mathbb{R}$ is a constant that comes from an effective microscopic model with hard-core constraints.

The gate for the crossover: the critical droplet

Target Theorem 2 [Critical droplet] For every $\kappa \in (1,\infty)$ and $\delta > 0$,

$$\lim_{\beta\to\infty} \mathbb{P}_{\square}\big(\tau_{\mathcal{C}_\delta(\kappa)} < \tau_{\blacksquare} \mid \tau_{\square} > \tau_{\blacksquare}\big) = 1, \quad \text{where}$$

$$\mathcal{C}_\delta(\kappa) = \Big\{\gamma \in \Gamma\colon\ \exists x \in \mathbb{T},\ B_{R_c(\kappa)-\delta}(x) \subset h(\gamma) \subset B_{R_c(\kappa)+\delta}(x)\Big\}$$



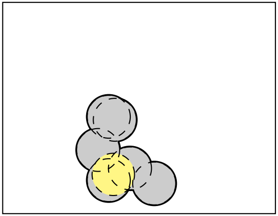
The critical droplet in the metastable regime is close to a disc of radius $R_c(\kappa)$ and has a random boundary.
$\asymp \beta$ disks in the interior,
$\asymp \beta^{1/3}$ disks on the boundary.

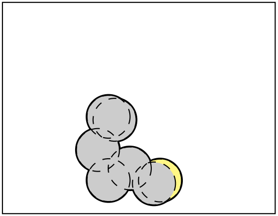
- $\Phi(\kappa)$ scales with β and is the volume free energy of the critical droplet
- $\Psi(\kappa)$ scales with $\beta^{1/3}$ and is the surface free energy of the critical droplet

Heuristics for volume free energy

In the metastable regime $z = \kappa z_c(\beta)$, $z_c(\beta) = \beta e^{-\pi\beta}$, the birth rate is

$$b(x, \gamma) = \kappa\beta\, e^{-\beta[V(\gamma \cup x) - V(\gamma)]}$$





- Particles inside a cluster are created at a rate $\kappa\beta$. $\Rightarrow$ Inside a droplet Poisson point process with intensity $\kappa\beta \gg 1$
- Particles sticking out are created at a rate exp small in "sticking out" area (yellow area), which is function of the local curvature. Particles that are sticking out are $\sim \beta^{1/3}$ and stick out of $\sim \beta^{-2/3}$

Our method: potential theoretic approach

Link between **mean metastable time** and **capacity**:

$$\mathbb{E}_{\square}(\tau_{\blacksquare}) = [1+o(1)]\,\frac{\mu_\beta(\square)}{\mathrm{cap}(\square,\blacksquare)}$$

(Bovier, Eckhoff, Gayrard and Klein, 2001; Bovier and den Hollander, 2015)

where the *capacity* of $\square, \blacksquare \subset \Gamma$ is defined as

$$\mathrm{cap}(\square,\blacksquare) = \mu_\beta(\square)\,\mathbb{P}_{\square}(\tau_{\blacksquare} < \tau_{\square}).$$

For the choice $z = \kappa\, z_c(\beta) = \kappa\,\beta\,\mathrm{e}^{-\beta\pi}$ the grand-canonical Gibbs measure reads

$$\mu_\beta(\mathrm{d}\gamma) = \frac{1}{\Xi_\beta}\,(\kappa\beta)^{N(\gamma)}\,\mathrm{e}^{-\beta V(\gamma)}\,\mathbb{Q}(\mathrm{d}\gamma)$$

Our method: potential theoretic approach

The capacity is given by two dual variational principles: the Dirichlet principle and the Thomson principle.

$$\mathrm{cap}(\square,\blacksquare) = \inf_{\substack{f:\ \Gamma\to[0,1] \\ f|_{\square}=1,\ f|_{\blacksquare}=0}} \mathcal{E}(f,f) = \sup_{\substack{f:\ \Gamma\to[0,1] \\ Lf\le 0 \text{ on } \Gamma\setminus(\square,\blacksquare)}} \frac{\mathcal{E}(\mathbf{1}_{\square},f)^2}{\mathcal{E}(f,f)},$$

where the Dirichlet form associated with the dynamics reads

$$\mathcal{E}(f,f) = \frac{1}{\Xi_\beta}\int_\Gamma \mathbb{Q}(\mathrm{d}\gamma)\int_\Lambda \mathrm{d}x\,(\kappa\beta)^{N(\gamma\cup x)}\,e^{-\beta V(\gamma\cup x)}\,\big[f(\gamma\cup x)-f(\gamma)\big]^2.$$

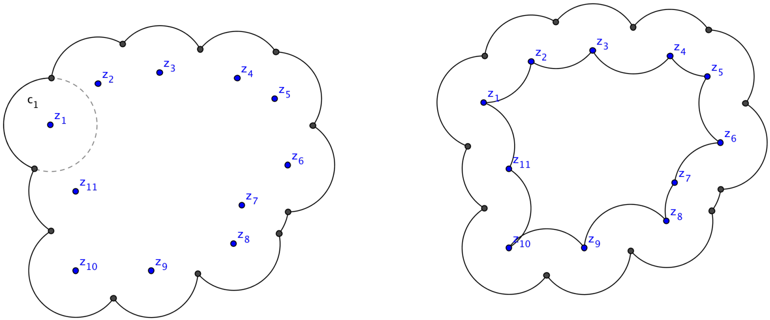
It turns out

$$\mathrm{cap}(\square,\blacksquare) = O(\beta)\mu_\beta\Big(|V(\gamma)-\pi R_c^2| \le C\beta^{-2/3}\Big) + s.o.t.$$

The main contribution to the capacity comes from the configurations where the volume of the halo is close to the volume of the critical disk.

Admissible halo shapes

Let S be a halo shape
Let $S^- = \{x \in S\colon\ B_1(x) \subset S\}$ be the 1-interior of S



Let $\mathcal{S}_\Lambda$ be the set of "admissible" halo shapes

Results I: LDP

Let $S^- = \{x \in S\colon\ B_1(x) \subset S\}$ be the 1-interior of S and $\mathcal{S}_\Lambda$ be the set of "admissible" halo shapes.

Theorem (Large deviation principle for the halo volume)

The family of probability measures $(\mu_\beta(V(\gamma) \in \cdot\,))_{\beta \geq 1}$ *satisfies the LDP on* $[0, \infty)$ *with speed* β *and with good rate function* I^* *given by*

$$I^*(A) = \inf\{I(S)\colon\ |S| = A\}, \qquad A \in [0, \infty),$$

where

$$I(S) = |S| - \kappa|S^-| - (1-\kappa)|\mathbb{T}|$$

Informally,

$$\mu_\beta\big(V(\gamma) \approx A\big) \approx \exp\big(-\beta I^*(A)\big).$$

[ideas from T. Schreiber, 2003; contraction principle]

Results II: isoperimetric inequality

Theorem (Minimisers of rate function for halo volume)

(1) *For every* $R \in (1, \frac{L}{\pi} + \frac{1}{2})$,

$$\min\left\{|S| - \kappa|S^-|\colon\ S \in \mathcal{S}, |S| = \pi R^2\right\} = \pi R^2 - \kappa\pi(R-1)^2$$

and the minimisers are the discs of radius R.

(2) *The minimisers are stable in the following sense: There exists an* $\varepsilon_0 > 0$ *such that if* $0 < \varepsilon < \varepsilon_0$ *and* $S \in \mathcal{S}$ *satisfies*

$$\big(|S| - \kappa|S^-|\big) - \big(\pi R^2 - \pi(R-1)^2\big) \leq \pi\kappa\varepsilon \quad \textit{with} \quad |S| = \pi R^2,$$

then S^- *is connected and simply connected, and*

$$d_{\mathrm{H}}(\partial S, \partial B_R) \leq \sqrt{5R\varepsilon},$$

where d_{H} *denotes the Hausdorff distance.*

[Bonnesen's strong isoperimetric inequality]

Recap of what we found so far

For every R, we have

$$I^*(\pi R^2) = I(B_R) = \Phi_\kappa(R) - (1-\kappa)|\mathbb{T}|.$$

To reach our target, we need to zoom in on a neighborhood of the critical droplet, i.e. $R = R_c$. The large deviation principle implies

$$\mu_\beta\Big(|V(\gamma) - \pi R_c^2| \le \varepsilon\Big) = \exp\Big(-\beta \min_{\substack{A\in[0,\infty):\\ |A-\pi R_c^2|\le\varepsilon}} I^*(A) + o(\beta)\Big), \qquad \beta\to\infty,$$

for $\varepsilon > 0$ fixed. We would like to take $\varepsilon = \varepsilon(\beta) \downarrow 0$, for which we need a refined analysis. We would like to capture the term of order $\beta^{1/3}$.

Remember: $\Phi_\kappa(R) = \pi R^2 - \kappa\pi(R-1)^2$

Moderate deviation and surface term

In particular, we want to compute the asymptotics of

$$\frac{1}{\beta^{1/3}} \log\Big\{ \mathrm{e}^{\beta I(B_{R_c})} \mu_\beta \Big(|V(\gamma) - \pi R_c^2| \le C\beta^{-2/3} \Big) \Big\}, \qquad \beta \to \infty.$$

This is done by controlling the mesoscopic fluctuations of the surface of the critical droplet.

Results III: mesoscopic fluctuations of the critical droplet

Theorem (Moderate deviation: rough asymptotics)

For C large enough,

$$\limsup_{\beta\to\infty} \frac{1}{\beta^{1/3}} \log\Big\{ e^{\beta I(B_{R_c})} \mu_\beta\Big(|V(\gamma) - \pi R_c^2| \le C\beta^{-2/3} \Big) \Big\} \le 2\pi G_\kappa \tau_*,$$

$$\liminf_{\beta\to\infty} \frac{1}{\beta^{1/3}} \log\Big\{ e^{\beta I(B_{R_c})} \mu_\beta\Big(|V(\gamma) - \pi R_c^2| \le C\beta^{-2/3} \Big) \Big\} \ge 2\pi G_\kappa (\tau_* - c),$$

with $c \in (0,\infty)$ some constant, $\tau_* \in \mathbb{R}$ solution of the equation

$$\int_0^\infty \sqrt{2\pi u}\, \exp\Big(-\tau_* u - \frac{u^3}{24} \Big)\, du = 1,$$

and

$$G_\kappa = \frac{(2\kappa)^{2/3}}{\kappa - 1}.$$

In order to have sharp asymptotics, we need to do better!

Results III: mesoscopic fluctuations of the critical droplet

Theorem (Moderate deviation: sharp asymptotics)

Under "certain assumptions", for C large enough and $\beta \to \infty$,

$$\mu_\beta\Big(|V(\gamma) - \pi R_c^2| \le C\beta^{-2/3}\Big) = e^{-\beta I(B_{R_c}) + \beta^{1/3}\Psi(\kappa) + o(\beta^{1/3})},$$

where, for some $\tau_{**} > 0$ that does not depend on κ,

$$I(B_{R_c}) = \Phi(\kappa) - (1-\kappa)|\mathbb{T}|, \qquad \Psi(\kappa) = 2\pi G_\kappa(\tau_* - \tau_{**}).$$

- The LD and MD theorems (sharp and rough asymptotics) are given in [1];
- The "certain assumptions" are related to the microscopic fluctuations of the surface of the critical droplet and come from an effective microscopic interface model. Their proof is given in [2].

[1] F. den Hollander, S. Jansen, R. Kotecký, E. Pulvirenti, "The Widom-Rowlinson model: Mesoscopic fluctuations for the critical droplet", preprint arXiv: 1907.00453 [math-ph]

[2] – –, "The Widom-Rowlinson model: Microscopic fluctuations for the critical droplet and effective interface model", in preparation

[3] – –, "The Widom-Rowlinson model: Metastability", in preparation

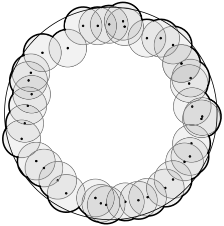
Proof: main ingredients

Few words on the proofs:

1. For the MD bounds:
   - parametrize the halo by its boundary points and reduce everything in terms of a surface integral.
   - find an expansion for the surface term in terms of polar coordinates.
   - reformulate in terms of auxiliary random variables: angular and radial coordinates described in terms of stochastic processes. This will capture the mesoscopic fluctuations of the boundary.
2. For the sharp MD result: rescale the random variables to zoom in and study an effective microscopic interface model. Prove that the conditions related to this new model hold true.

Some details on the proof:

(1) Parametrize the halo by its boundary points:



Given S, $z_1, \dots, z_N$ are the boundary points of S, where N is random.

$$\int_\Gamma \mathbb{Q}(\mathrm{d}\gamma) \longrightarrow \int_{\mathbb{T}^N} \mathrm{d}z_1 \cdots \mathrm{d}z_N \mathbf{1}_{\{z \text{ are boundary points}\}}$$

Key step: Reduction to a surface integral

$$\mu_\beta\Big(h(\gamma) \in A\Big)$$
$$= \left[1 - O(\mathrm{e}^{-c\beta})\right] e^{-\beta I^*(\pi R_c^2)} \sum_{n \in \mathbb{N}_0} \frac{(\kappa\beta)^n}{n!} \int^*_{\mathbb{T}^n} \mathrm{d}z \, \mathrm{e}^{-\beta \Delta(z)} \mathbf{1}_{\{S(z) \in A\}},$$

with $\Delta(z) = |S(z)| - \kappa|S^-(z)| - I^*(\pi R_c^2)$, where $\int^*$ runs over all the admissible *collections of boundary points*.

Mesoscopic fluctuations and surface term

(2) Find an expansion for the surface term:

$$\sum_{n\in\mathbb{N}_0} \frac{(\kappa\beta)^n}{n!} \int_{\mathbb{T}^n}^{*} \mathrm{d}z \; \mathrm{e}^{-\beta\Delta(z)} \, \mathbf{1}_{\mathcal{A}}(z),$$

$\Delta(z) = |S(z)| - \kappa|S^-(z)| - I^*(\pi R_c^2)$ and $\mathcal{A}$ the collection of all the constraints.

The way to go: Use polar coordinates: $z_i = \Big(r_i \cos t_i, r_i \sin t_i\Big)$, $r_i = \rho_i + R_c - 1$,

Expand $\Delta(z)$ and $\mathcal{A}$ in terms of ρ_i and t_i and write $(*)$ in terms of an expectation of functionals of random variables.

Auxiliary Point Processes:

- $\{t_i\}_{i=1}^n \to \mathcal{T}$ Poisson point process on $[0, 2\pi)$ w. intensity $\lambda(\beta) \sim \beta^{1/3}$
- $n \to N = |\mathcal{T}|$ Poisson random variable with parameter $2\pi\lambda(\beta)$
- $\{\rho_i\}_{i=1}^n \to \left\{\frac{B_{T_i}}{\sqrt{\beta}}\right\}$, where $(B_t)_{t\in[0,2\pi]}$ mean centered Brownian Bridge

Analysis via Large Deviations, ...

The microscopic interface model

$$\mathcal{Z}_L = \sum_{n\in\mathbb{N}_0} \int_{[0,L]^n} \mathrm{d}t_1 \cdots \mathrm{d}t_n \, \mathbf{1}_{\{0<t_1<\cdots<t_n<L\}} \int_{\mathbb{R}^{n+1}} \mathrm{d}\varphi_1 \cdots \mathrm{d}\varphi_{n+1}$$
$$\times \mathbf{1}_{\mathcal{E}}\big(\{t_j,\varphi_j\}_{j=0}^{n+1}\big) \exp\Big(-\sum_{i=1}^{n+1}(t_i-t_{i-1})^3 - \sum_{i=1}^{n+1}\frac{(\varphi_i-\varphi_{i-1})^2}{2(t_i-t_{i-1})}\Big),$$

with $t_0=0$, $t_{n+1}=L$ and $\varphi_0=0$, and where $\mathcal{E}$ is the set of configurations such that every $(t,\varphi)\in\mathcal{X}$ is extremal in $\mathcal{X}$.

The model is a modification of the one-dimensional Gaussian free field, where the lattice $\mathbb{Z}$ is replaced by a random point configuration on the interval $[0,L]$, and the set $\mathcal{E}$ constitutes a hard-core multi-body constraint.

Key result: *The location of each boundary point is constrained by the location of the two neighbouring boundary points only.*

Thank you for your attention!