LECTURE 9

Widom-Rowlinson model for disks in the plane

§ TARGET

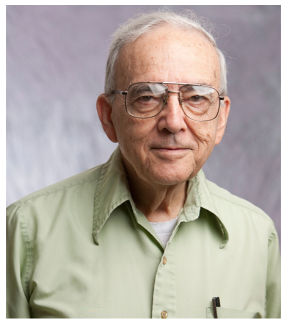
Our target is to describe metastability associated with condensation from a vapour to a liquid in the continuum.

In Lectures 9-11 we will look at a model of interacting disks in $\mathbb{R}^2$ and put forward a detailed picture of how a super-saturated vapour undergoes a metastable crossover to a liquid.

In Lecture 12 we will speculate what happens when we go to higher dimensions, and to a model where the disks are replaced by arbitrary compact convex grains.

granular media

In Lectures 9–11 we focus on the Widom-Rowlinson model of interacting disks in the plane.



In the continuum, all questions about phase transitions, critical behaviour and metastability turn out to be much more challenging than on lattices and graphs.

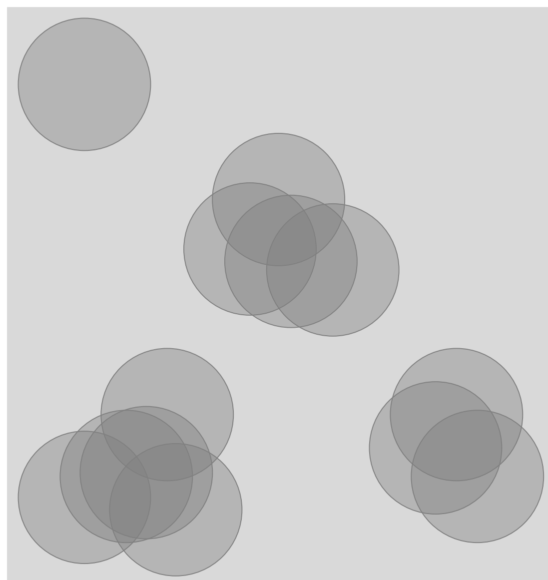
In the Widom-Rowlinson model, the interactions are purely geometric, which makes it more tractable.

F. den Hollander, S. Jansen, R. Kotecký, E. Pulvirenti
work in progress

§ THE STATIC WIDOM-ROWLINSON MODEL

Let $\mathbb{T} \subset \mathbb{R}^2$ be a finite torus. The set of finite particle configurations in $\mathbb{T}$ is

$$\Gamma = \{\gamma \subset \mathbb{T} \colon N(\gamma) \in \mathbb{N}_0\}, \quad N(\gamma) = \text{ cardinality of } \gamma.$$



disks of radius 1 around γ

The grand-canonical Gibbs measure is

$$\mu(\mathrm{d}\gamma) = \frac{1}{\Xi} z^{N(\gamma)} \,\mathrm{e}^{-\beta H(\gamma)} \mathbb{Q}(\mathrm{d}\gamma),$$

where

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

H is the interaction Hamiltonian given by

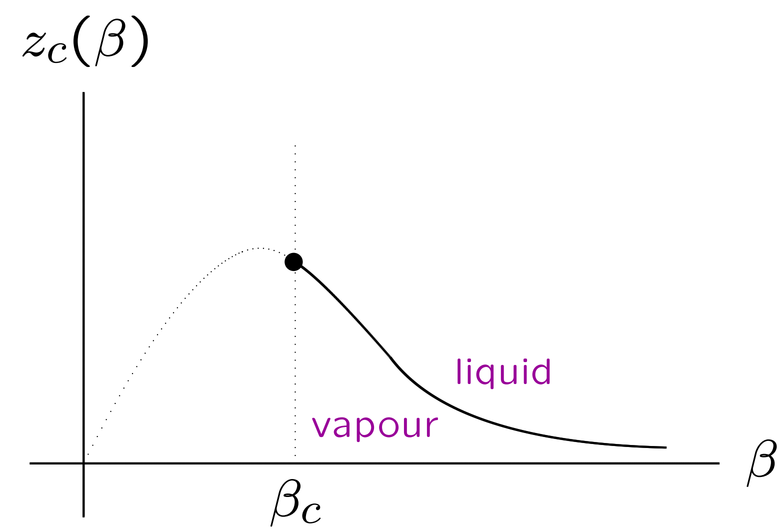
$$H(\gamma) = \Big| \bigcup_{x \in \gamma} B(x) \Big| - \sum_{x \in \gamma} |B(x)|,$$

i.e., minus the total overlap of the disks of radius 1 around γ. This makes the interaction attractive.

For $\beta > \beta_c$ a phase transition occurs at

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

in the thermodynamic limit, i.e., $\mathbb{T} \to \mathbb{R}^2$. No closed form expression is known for β_c.

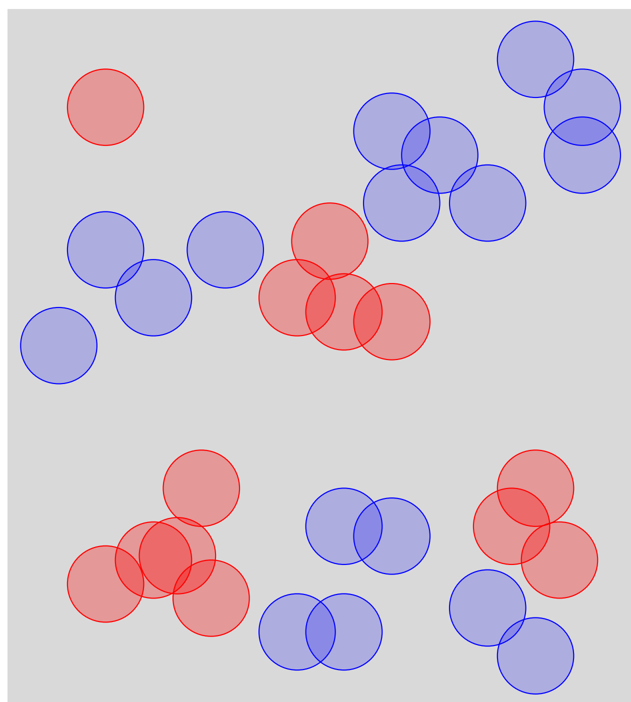


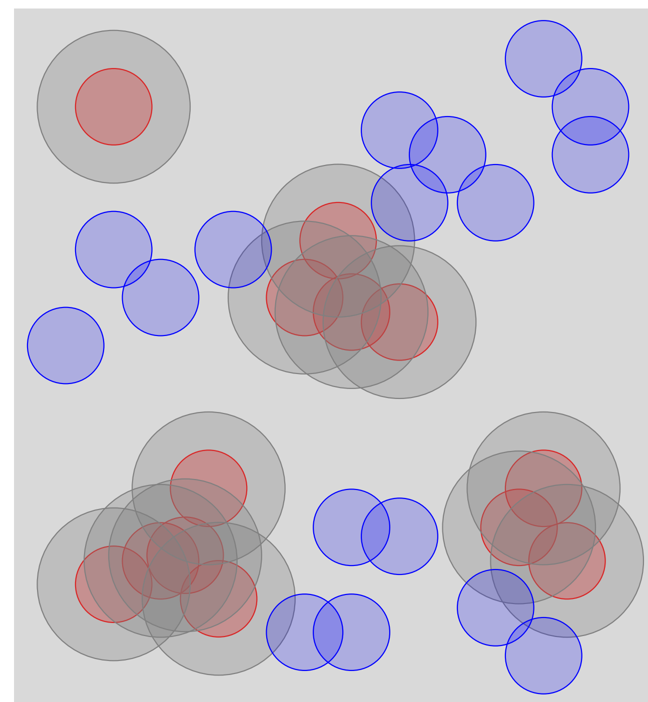
Ruelle 1971

Lebowitz, Gallavotti 1971

Chayes, Chayes, Kotecký 1995

The one-species model can be seen as the projection of a two-species model with hard-core repulsion:





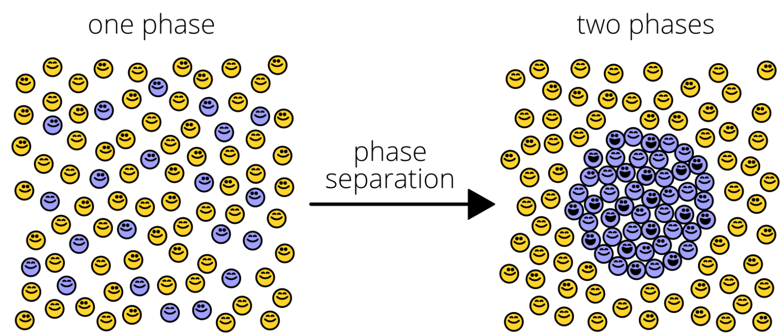
Disks of radius $\frac{1}{2}$ around γ^{red} and γ^{blue} with chemical activities z^{red} and z^{blue}.

EXERCISE!

The hard-core repulsion in the two-species model implies that the centers of the disks of one species must stay outside the halo of radius 1 around the centers of the disks of the other species.

When we integrate out over one species, we precisely get the Widom-Rowlinson interaction for the other species.

The crossover in the one-species model from vapour to liquid corresponds to a phase separation of species in the two-species model.



§ THE DYNAMIC WIDOM-ROWLINSON MODEL

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

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

i.e., particles are born at rate b and die at rate d, given by a heat bath dynamics

$$\begin{aligned} b(x,\gamma) &= z\,\mathrm{e}^{-\beta[H(\gamma\cup x)-H(\gamma)]}, & x \notin \gamma, \\ d(x,\gamma) &= 1, & x \in \gamma. \end{aligned}$$

The grand-canonical Gibbs measure is the unique reversible equilibrium of this stochastic dynamics.

particles do not move!

KEY QUESTION:

Let $\square$ and $\blacksquare$ denote the set of configurations where $\mathbb{T}$ is empty, respectively, full.

- Start with $\mathbb{T}$ empty, i.e., $\gamma_0 = \square$.
  [preparation in vapour state]
- Choose $z = \kappa z_c(\beta)$, $\kappa \in (1, \infty)$.
  [reservoir is super-saturated vapour]
- Wait for the first time $\tau_{\blacksquare}$ when the system fills $\mathbb{T}$.
  [condensation to liquid state]

$$\boxed{\text{What can be said about the law of } \tau_{\blacksquare} \text{ in the limit as } \beta \to \infty \text{ for fixed } \mathbb{T} \text{ and } \kappa?}$$

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

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

and the Dirichlet form associated with the dynamics reads

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

where $N(\gamma)$ is the cardinality of γ and $V(\gamma)$ is the volume of the halo of γ.

Both quantities play a crucial role for the computation of capacities that underpin the potential-theoretic approach to metastability. Recall that the Dirichlet principle gives

$$\boxed{\mathrm{cap}(\square,\blacksquare) = \inf_{\substack{f\colon \Gamma\to[0,1] \\ f|_{\square}=1,\, f|_{\blacksquare}=0}} \mathcal{E}(f,f)}$$

and that

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

in the metastable regime.

Our task is to approximate

$$\Xi\,\mathcal{E}(f,f) = \int_{\Gamma} \mathbb{Q}(\mathrm{d}\gamma) \int_{\mathbb{T}} \mathrm{d}x\,(\kappa\beta)^{N(\gamma\cup x)}\,\mathrm{e}^{-\beta V(\gamma\cup x)} \times \Big[f(\gamma\cup x) - f(\gamma)\Big]^2,$$

by inserting test functions f that are close to the unique minimiser $f = h_{\square,\blacksquare}$. In this way we obtain the desired asymptotics of $\Xi\mathrm{cap}(\square,\blacksquare)$ and hence of $\mathbb{E}_{\square}(\tau_{\blacksquare})$.

Note that $\mathbb{Q}(\square) = \mathrm{e}^{-|\mathbb{T}|}$ does not depend on the relevant parameters κ,β.

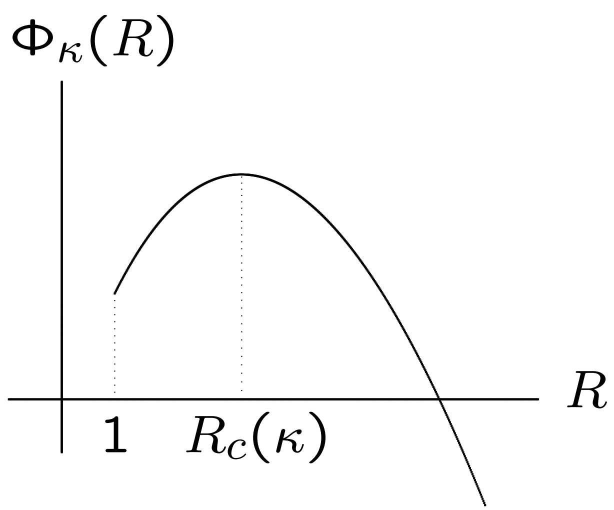
HEURISTICS:

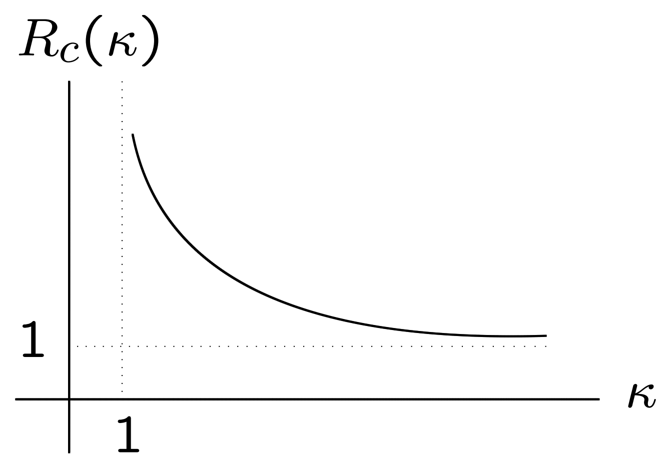
- Since particles have a tendency to stick together, they form a droplet that is close to a disk, say of radius R.
- Inside the droplet, particles are distributed according to a Poisson process with intensity $\kappa\beta \gg 1$.
- Near the perimeter of the droplet, particles are born at a rate that depends on how much they stick out.
- For small R the droplet tends to shrink, for large R it tends to grow. The curvature of the droplet determines which of the two prevails.

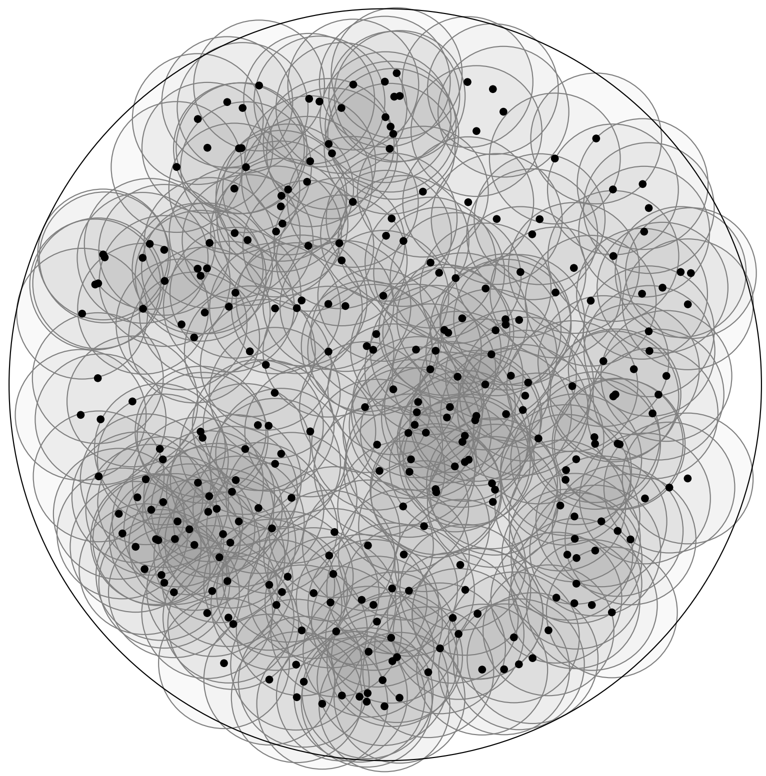
§ THREE THEOREMS

For $R \in [1, \infty)$ and $\kappa \in (1, \infty)$, let

$$\Phi_\kappa(R) = \pi R^2 - \kappa\pi(R-1)^2, \qquad R_c(\kappa) = \frac{\kappa}{\kappa - 1}.$$







A critical droplet of radius $R_c(\kappa)$ filled with 1-disks:

$\asymp \beta$ disks in the interior, $\asymp \beta^{1/3}$ disks on the boundary

Stillinger, Weeks 1995

capillary waves

THEOREM 9.1 [Arrhenius formula]

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

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

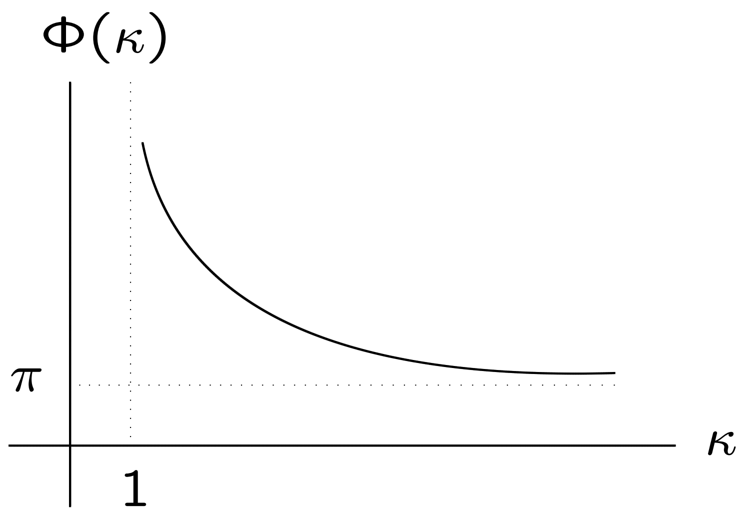
where

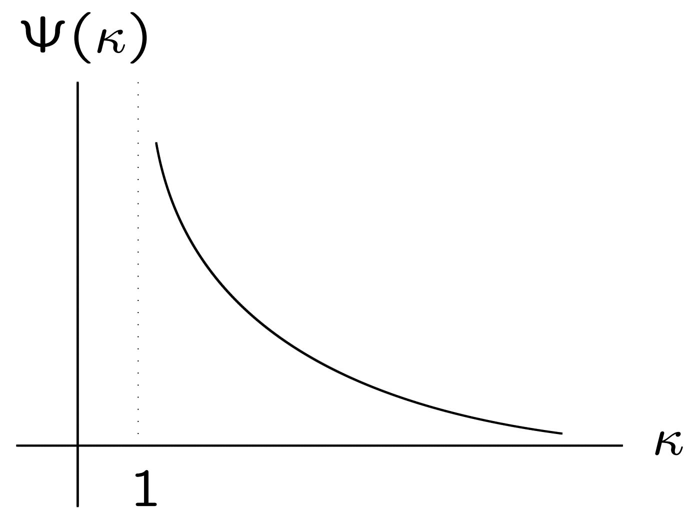
$$\Phi(\kappa) = \Phi_\kappa(R_c(\kappa)) = \frac{\pi\kappa}{\kappa - 1},$$

$$\Psi(\kappa) = \Psi_\kappa(R_c(\kappa)) = s_*\,\frac{\kappa^{2/3}}{\kappa - 1},$$

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

Plots of the key quantities in the Arrhenius formula:





$$\boxed{\begin{array}{l}\Phi(\kappa) = \text{volume free energy critical droplet}\\ \Psi(\kappa) = \text{surface free energy critical droplet}\end{array}}$$

EXERCISE!

THEOREM 9.2 [Exponential law]

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

$$\lim_{\beta \to \infty} \mathbb{P}_{\square}\Big(\tau_{\blacksquare} / \mathbb{E}_{\square}(\tau_{\blacksquare}) > t\Big) = \mathrm{e}^{-t} \qquad \forall\, t \geq 0.$$

The exponential law is typical for metastable crossover times: the critical droplet appears after many unsuccessful attempts.

For $\delta > 0$, let

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

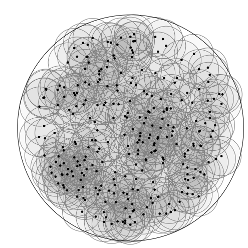
THEOREM 9.3 [Critical droplet]

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

$$\lim_{\beta\to\infty} \mathbb{P}_\square\Big(\tau_{\mathcal{C}_{\delta(\beta)}(\kappa)} < \tau_\blacksquare \,\Big|\, \tau_\square > \tau_\blacksquare\Big) = 1$$

when

$$\lim_{\beta\to\infty} \delta(\beta) = 0, \qquad \lim_{\beta\to\infty} \beta^{2/3}\delta(\beta) = \infty.$$



The estimation of the Dirichlet form requires an evaluation of high-dimensional surface integrals. The details of the computation are rather delicate:

variational principles
isoperimetric inequalities
volume large deviations
surface moderate deviations
microscopic hard-core Gibbs measures
mesoscopic capillary waves
coarse-graining techniques
capacities estimates
...

In Lectures 10-11 we will discuss the key ingredients.

EXERCISE!

We know from Lectures 2–3 that the test function f we must pick to approximate the unique minimiser $f = h_{\blacksquare,\square}$ of

$$\Xi\,\mathcal{E}(f,f) = \int_\Gamma \mathbb{Q}(\mathrm{d}\gamma) \int_\mathbb{T} \mathrm{d}x\,(\kappa\beta)^{N(\gamma\cup x)}\,\mathrm{e}^{-\beta V(\gamma\cup x)} \times \Big[f(\gamma\cup x) - f(\gamma)\Big]^2$$

is such that

$$f(\gamma) \approx \begin{cases} 0, & \gamma \in V_\blacksquare, \\ 1, & \gamma \in V_\square, \\ f^*(\gamma), & \Gamma \setminus (V_\blacksquare \cup V_\square), \end{cases}$$

where $V_\blacksquare$ and $V_\square$ are the valleys around $\blacksquare$ and $\square$, which are separated by a neighbourhood of the critical droplet, and f^* is a test function on that neighbourhood, which depends on both the volume and the surface of the critical droplet.

§ CONCLUSION

We have obtained a detailed description of metastability for a model of interacting particles in the continuum.

The Arrhenius formula for the average condensation time involves both the volume free energy and the surface free energy of the critical droplet.

There are many challenges in understanding the details behind the droplet formation.

PAPERS:

F. den Hollander, S. Jansen, R. Kotecký and E. Pulvirenti:

(1) *The Widom-Rowlinson model: Metastability.*
In progress.

(2) *The Widom-Rowlinson model: Mesoscopic fluctuations for the critical droplet.*
Preprint 2019 [arXiv:1907.00453].

(3) *The Widom-Rowlinson model: Microscopic fluctuations for the critical droplet.*
In progress.