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Large Deviations for Cluster Size Distributions in a Classical Many-Body System

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Background and Goals

- We consider a classical stable interacting many-particle system with attraction in continuous space.
- Objective: study the transition between gaseous and solid phase in the thermodynamic limit.
- Very difficult at positive temperature and positive particle density.
- Instead, we study a dilute low-temperature regime. This makes the particles organise themselves into small groups called clusters.
- We approximate the system with a well-known ideal-mixture of clusters (droplets) and prove that the difference vanishes exponentially with vanishing temperature.
- We study
  - the free energy,
  - the constrained free energy given a cluster-size distribution,
  - the optimal cluster-size distribution.

Energy

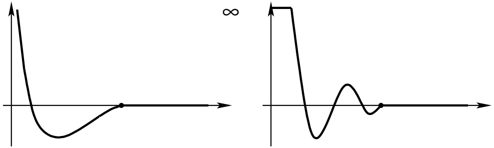
Energy of N particles in $\mathbb{R}^d$:

$$U_N(x) = U_N(x_1,\dots,x_N) = \sum_{\substack{i,j=1\\ i\neq j}}^{N} v\big(|x_i - x_j|\big), \qquad \text{for } x=(x_1,\dots,x_N)\in(\mathbb{R}^d)^N.$$

Pair-interaction function $v\colon [0,\infty) \to (-\infty,\infty]$ of Lennard-Jones type:

Lennard-Jones potential

$v(r) = r^{-12} - r^{-6}$



examples of our potentials

- short-distance repulsion (possibly hard-core) implying stability,
- preference of a certain positive distance,
- bounded interaction length.

inverse temperature $\beta \in (0,\infty)$

Gibbs measure: $$\mathbb{P}^{(N)}_{\beta,\Lambda}(\mathrm{d}x) = \frac{1}{Z_\Lambda(\beta,N)N!}\mathrm{e}^{-\beta U_N(x)}\,\mathrm{d}x, \qquad x \in \Lambda^N.$$

Partition function: $$Z_\Lambda(\beta,N) = \frac{1}{N!}\int_{\Lambda^N} \mathrm{e}^{-\beta U_N(x)}\,\mathrm{d}x.$$

Connectivity structure: Fix R larger than the interaction length of v.
Sites x and y are called connected if $|x-y| \leq R$.
clusters (droplets) $=$ the connected components
$N_k(x) =$number of k-clusters in $x = (x_1,\dots,x_N)$

k-cluster density : $$\rho_{k,\Lambda}(x) = \frac{N_k(x)}{|\Lambda|}$$

cluster size distribution: $$\rho_\Lambda = \big(\rho_{k,\Lambda}\big)_{k\in\mathbb{N}}$$

as an $M_{N/|\Lambda|}$-valued random variable, where

$$M_\rho := \Big\{(\rho_k)_{k\in\mathbb{N}} \in [0,\infty)^{\mathbb{N}} \,\Big|\, \sum_{k\in\mathbb{N}} k\rho_k \leq \rho\Big\}, \qquad \rho \in (0,\infty).$$

Regimes Considered

We study the cluster-size distribution in the box $\Lambda = [0,L]^d$

- in the thermodynamic limit

$$N \to \infty, \qquad L = L_N \to \infty, \qquad \text{such that } \frac{N}{L_N^d} \to \rho \in (0,\infty),$$

followed by the dilute low-temperature limit

$$\beta \to \infty, \rho \downarrow 0 \qquad \text{such that } -\frac{1}{\beta} \log \rho \to \nu \in (0,\infty),$$

(joint work with SABINE JANSEN and BERND METZGER, WIAS.)

- and in the coupled dilute low-temperature limit

$$N \to \infty, \qquad \beta = \beta_N \to \infty, \qquad L = L_N \to \infty \qquad \text{such that } -\frac{1}{\beta_N} \log \frac{N}{L_N^d} \to \nu \in (0,\infty).$$

(joint work with A. COLLEVECCHIO (Venice), P. MÖRTERS (Bath) and N. SIDOROVA (London))

Here,

- total entropy $\approx$ sum of the entropies of the clusters,
- excluded-volume effect between the clusters may be neglected,
- mixing entropy may be neglected.

LDP in the Thermodynamic Limit

Free energy per unit volume : $$f_\Lambda(\beta, \tfrac{N}{|\Lambda|}) := -\frac{1}{\beta|\Lambda|}\log Z_\Lambda(\beta, N).$$

limiting free energy : $$f(\beta,\rho) := \lim_{\substack{N,L\to\infty\\ N/L^d\to\rho}} f_{[0,L]^d}(\beta, \tfrac{N}{L^d}).$$

Goal: find $f(\beta,\rho,\cdot)\colon M_\rho \to [0,\infty]$ such that

$$\frac{1}{N!}\int_{\Lambda^N} \mathrm{e}^{-\beta U_N(x)} 1\!\!1\Big\{(\rho_{k,\Lambda}(x))_{k\in\mathbb{N}} \approx (\rho_k)_{k\in\mathbb{N}}\Big\}\,\mathrm{d}x \approx \exp\Big(-\beta|\Lambda|\, f(\beta,\rho,(\rho_k)_{k\in\mathbb{N}})\Big),$$

and define the rate function as

$$J_{\beta,\rho}\big((\rho_k)_{k\in\mathbb{N}}\big) = \beta\big(f(\beta,\rho,(\rho_k)_{k\in\mathbb{N}}) - f(\beta,\rho)\big).$$

Large deviation principle with convex rate function, [JKM11]

In the thermodynamic limit $N\to\infty$, $L\to\infty$, $N/L^d\to\rho$, the distribution of ρ_Λ under $\mathbb{P}^{(N)}_{\beta,\Lambda}$ with $\Lambda=[0,L]^d$ satisfies a large deviation principle with speed $|\Lambda| = L^d$. The rate function $J_{\beta,\rho}\colon M_{\rho+\varepsilon}\to[0,\infty]$ is convex, and its effective domain $\{J_{\beta,\rho}(\cdot)<\infty\}$ is contained in M_ρ.

On the Proof of the LDP

Standard strategy, adapted to cluster-size distributions:

1. Projection: LDP for $(\rho_{k,\Lambda}(x))_{k=1,\dots,j}$ for fixed j with some rate function $J_{\beta,\rho,j}$.
   - Use subadditivity along special seqences of increasing cubes (having a separating margin) to define a densely defined preliminary rate function,
   - extend this rate function continuously and prove that it is finite on open sets,
   - fill the gaps for an arbitrary sequence of cubes,
   - show that the extended preliminary rate function gives an LDP.
2. Apply the Gärtner-Dawson theorem (projective limit LDP) to get full LDP with rate function

$$J_{\beta,\rho}\big((\rho_k)_{k\in\mathbb{N}}\big)=\sup_{j\in\mathbb{N}} J_{\beta,\rho,j}\big((\rho_k)_{k=1,\dots,j}\big).$$

Dilute Low-Temperature Limit

The ground state, i.e., zero temperature : $\quad E_N := \inf_{x \in (\mathbb{R}^d)^N} U_N(x).$

stability & subadditivity $\quad \Longrightarrow \quad e_\infty := \lim_{N\to\infty} \frac{E_N}{N} \in (-\infty, 0)$ exists.

Interpret $q_k = k\rho_k/\rho$ as the probability that a given particle lies in a k-cluster.

Approximate rate function: $\quad g_\nu\big((q_k)_k\big) := \sum_{k\in\mathbb{N}} q_k \frac{E_k - \nu}{k} + \Big(1 - \sum_{k\in\mathbb{N}} q_k\Big) e_\infty$

on the set

$$\mathscr{Q} := \Big\{ (q_k)_{k\in\mathbb{N}} \in [0,1]^{\mathbb{N}} \,\Big|\, \sum_{k\in\mathbb{N}} q_k \le 1 \Big\}$$

Γ-convergence of the rate function, [JKM11]

In the limit $\beta \to \infty$, $\rho \to 0$ such that $-\beta^{-1}\log\rho \to \nu$, the function

$$\mathscr{Q} \to \mathbb{R} \cup \{\infty\}, \qquad (q_k)_k \mapsto \frac{1}{\rho} f\Big(\beta, \rho, (\tfrac{\rho q_k}{k})_{k\in\mathbb{N}}\Big)$$

Γ-converges to g_ν.

Explanation

Our Approximations:

- We approximate $f(\beta, \rho, (\rho_k)_k)$ by an ideal gas of clusters, neglecting the "excluded volume":

$$f^{\text{ideal}}(\beta, \rho, (\rho_k)_k) := \sum_{k\in\mathbb{N}} k\rho_k f_k^{\text{cl}}(\beta) + \Big(\rho - \sum_{k\in\mathbb{N}} k\rho_k\Big) f_\infty^{\text{cl}}(\beta) + \frac{1}{\beta}\sum_{k\in\mathbb{N}} \rho_k(\log\rho_k - 1).$$

  ($f_k^{\text{cl}}(\beta) =$ free energy per particle in a cluster of size k.)

- We approximate $f^{\text{ideal}}(\beta, \rho, (\frac{\rho q_k}{k})_{k\in\mathbb{N}})$ with $\rho g_\nu(q)$ using two simplifications:
  - cluster internal free energies $\approx$ ground state energies: $f_k^{\text{cl}}(\beta) \approx E_k$.
  -

$$\frac{1}{\beta}\sum_{k\in\mathbb{N}} \rho_k(\log\rho_k - 1) = \sum_{k\in\mathbb{N}} \rho_k \frac{\log\rho}{\beta} + \frac{\rho}{\beta}\sum_{k\in\mathbb{N}} \frac{q_k}{k}\Big(\log\frac{q_k}{k} - 1\Big) \approx \sum_{k\in\mathbb{N}} \rho_k \frac{\log\rho}{\beta}$$
$$\approx -\rho \sum_{k\in\mathbb{N}} q_k \frac{\nu}{k}.$$

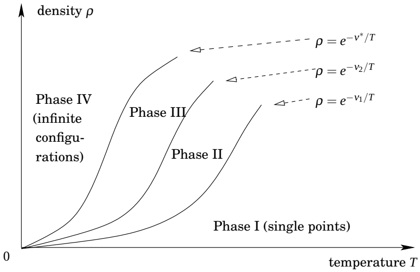
In classical statistical physics: "Geometric (or droplet) picture of condensation".

Closely related to the contour picture of the Ising model an lattice gases.

Consequences of Γ-convergence, [JKM11]

In the same limit $\beta \to \infty$, $\rho \downarrow 0$ such that $-\frac{1}{\beta}\log\rho \to \nu$,

- $$\frac{1}{\rho} f(\beta,\rho) \to \min_{\mathcal{Q}} g_\nu =: \mu(\nu),$$
- if ν is not a kink point of $\mu(\cdot)$, then any minimiser of $J_{\beta,\rho}$ converges to the minimiser of g_ν.



Properties of g_ν

- $\nu^* := \inf_{N\in\mathbb{N}}(E_N - Ne_\infty)$ lies in $(0,\infty)$.
- $\nu \mapsto \mu(\nu) = \inf_{\mathcal{Q}} g_\nu = \inf_{N\in\mathbb{N}} \frac{E_N-\nu}{N}$ is continuous, piecewise affine and concave.
- $\mu(\cdot)$ has at least one kink, and the kinks accumulate at most at ν^*.
- If $\nu \in (\nu^*,\infty)$ is not a kink point, then g_ν has the unique minimizer $\delta_{k(\nu)}$ (Dirac sequence) with $k(\nu)$ the unique minimizer of $k \mapsto (E_k - \nu)/k$.
- For $\nu < \nu^*$, the unique minimizer of g_ν is 0 (zero sequence).

Interpretation:

- There is at least one phase transition, possibly much more.
- In the high-temperature phase $\nu \gg 1$, all clusters are singletons.
- In any intermediate phase, all clusters have size $k(\nu)$.
- In the low-temperature phase $\nu \in (0,\nu^*)$, there are only infinite clusters.

Corollary: LLN for Cluster Sizes

The main consequence of the LDP, together with the Γ-convergence of the rate function, is:

Limiting distributions of cluster sizes, [JKM11]

Let $\nu \in (0,\infty)$ be not a kink point, and fix $\varepsilon > 0$. Then, if β is sufficiently large, ρ sufficiently small and $-\frac{1}{\beta}\log\rho$ is sufficiently close to ν, for boxes Λ_N with volume N/ρ,

$$\begin{aligned} \lim_{N\to\infty} \mathbb{P}^{(N)}_{\beta,\Lambda_N}\Big(\Big|\frac{k(\nu)}{\rho}\rho_{k(\nu),\Lambda}-1\Big|>\varepsilon\Big) &= 0 \qquad \text{if } \nu > \nu^*, \\ \lim_{N\to\infty} \mathbb{P}^{(N)}_{\beta,\Lambda_N}\Big(\sum_{k\in\mathbb{N}}\rho_{k,\Lambda}>\varepsilon\Big) &= 0 \qquad \text{if } \nu < \nu^*. \end{aligned}$$

In other words, in this two-step limit, the model has only one cluster size, which is infinite for small ν.

Approximation with Ideal Mixture

- The approximation with g_ν is difficult to interpret physically, and g_ν has some "unphysical" properties: possibly many phase transitions of $\nu \mapsto \mu(\nu)$, and many minimisers of g_ν in the kinks. We think that just one of these phase transitions is "physical", the others correspond to cross-overs inside the gas phase.
- Much better is the approximation with the ideal mixture of droplets, f^{ideal}, which is known, under reasonable assumptions, to have only one phase transition.
- These assumptions are on the compactness of the shape of the relevant configurations at positive, but low temperature:
  - The main contribution to the cluster internal energy comes from compact (d-dimensional) configurations,
  - the correction term in the convergence $f_k^{\mathrm{cl}}(\beta) \to f_\infty^{\mathrm{cl}}(\beta)$ is of surface order: $k f_k^{\mathrm{cl}}(\beta) - k f_\infty^{\mathrm{cl}}(\beta) \geq C k^{1-1/d}$.

  (Verification seems out of reach yet.)
- We have rigorous bounds for the comparison of the original model with the ideal-mixture model, which are exponentially small in vanishing temperature, see next slides.

The ideal mixture

Recall:

$$f^{\mathrm{ideal}}(\beta,\rho,(\rho_k)_k) := \sum_{k\in\mathbb{N}} k\rho_k f_k^{\mathrm{cl}}(\beta) + \Big(\rho - \sum_{k\in\mathbb{N}} k\rho_k\Big) f_\infty^{\mathrm{cl}}(\beta) + \frac{1}{\beta}\sum_{k\in\mathbb{N}} \rho_k(\log\rho_k - 1).$$

- saturation density: Let

$$\rho_{\mathrm{sat}}^{\mathrm{ideal}}(\beta) := \sum_{k\in\mathbb{N}} k\,\mathrm{e}^{\beta k[f_\infty^{\mathrm{cl}}(\beta)-f_k^{\mathrm{cl}}(\beta)]} \in (0,\infty]$$

- chemical potential: For $\rho < \rho_{\mathrm{sat}}^{\mathrm{ideal}}(\beta)$, let $\mu^{\mathrm{ideal}}(\beta,\rho) \in (-\infty, f_\infty^{\mathrm{cl}}(\beta))$ be the unique solution of

$$\sum_{k=1}^{\infty} k\,\mathrm{e}^{\beta k[\mu^{\mathrm{ideal}}(\beta,\rho)-f_k^{\mathrm{cl}}(\beta)]} = \rho,$$

  and for $\rho \geq \rho_{\mathrm{sat}}^{\mathrm{ideal}}(\beta)$, let $\mu^{\mathrm{ideal}}(\beta,\rho) := f_\infty^{\mathrm{cl}}(\beta)$.

- Then, the minimiser $(\rho_k^{\mathrm{ideal}}(\beta,\rho))_k$ of $f^{\mathrm{ideal}}(\beta,\rho,\cdot)$ is given by

$$\rho_k^{\mathrm{ideal}}(\beta,\rho) = \mathrm{e}^{\beta k[\mu^{\mathrm{ideal}}(\beta,\rho)-f_k^{\mathrm{cl}}(\beta)]}.$$

- Under appropriate bounds on $f_k^{\mathrm{cl}}(\beta)$, the saturation density is finite at low temperature, and $f^{\mathrm{ideal}}(\beta,\rho,\cdot)$ has a phase transition.

Comparison with ideal mixture

Joint work with SABINE JANSEN (WIAS). Our hypotheses:

(1) Some Hölder continuity and uniform stability of v. (holds under general assumptions)

(2) Compact shape of ground states. (in $d \leq 2$ see [AU YEUNG, FRIESECKE, SCHMIDT (2011)])

(3) Compact shape of clusters at low temperature. (open)

(4) Surface-order correction: $k f_k^{\mathrm{cl}}(\beta) - k f_\infty^{\mathrm{cl}}(\beta) \geq C k^{1-1/d}$. (open)

Let $H(a;b) = \sum_{k\in\mathbb{N}} (b_k - a_k + a_k \log \frac{a_k}{b_k})$ denote the entropy.

Approximation with ideal mixture

Under Hypotheses (1), (3) and (4), for any sufficiently large β and sufficiently small ρ,

$$0 \leq f(\beta,\rho) - f^{\mathrm{ideal}}(\beta,\rho) \leq \frac{C}{\beta} m^{\mathrm{ideal}}(\beta,\rho)\rho^{1/(d+1)},$$

and, for any minimiser $\rho = \rho^{(\beta,\rho)} = (\rho_k)_{k\in\mathbb{N}}$ of $f(\beta,\rho,\cdot)$, with $m := \sum_{k\in\mathbb{N}} \rho_k$,

$$\Big|\frac{m}{m^{\mathrm{ideal}}(\beta,\rho)} - 1\Big|^2 \leq C'\rho^{1/(d+1)} \qquad \text{and} \qquad \frac{1}{2} H\Big(\frac{\rho}{m}; \frac{\rho^{\mathrm{ideal}}(\beta,\rho)}{m^{\mathrm{ideal}}(\beta,\rho)}\Big) \leq C'\rho^{1/(d+1)}.$$

If Hypotheses (3) and (4) are replaced by (2), this holds for $-\beta^{-1}\log\rho > v^* + \varepsilon$ with ε-dependent constants.

Coupled Limit

Idea: Couple inverse temperature $\beta = \beta_N \to \infty$ with particle density $N/L_N^d = \rho_N \to 0$ such that

$$-\frac{1}{\beta_N} \log \frac{N}{L_N^d} = \nu \in (0,\infty) \qquad \text{is constant.}$$

(Example: $\beta_N \asymp \log N$ and $|\Lambda_N| = |[0,L_N]^d = N^\alpha$ with $\alpha > 1$.)

Then energic and entropic forces compete on the same, critical scale, and determine the behaviour of the system.

Large $\nu \implies$ entropy wins, i.e., typical inter-particle distance diverges,
Small $\nu \implies$ interaction wins, i.e., crystalline structure in the particles emerges.

Free energy per particle in the coupled limit, [CKMS10]

$$-\mu(\nu) = \lim_{N\to\infty} \frac{1}{N\beta_N} \log Z_{[0,L_N]}(\beta_N, N).$$

On the Proof: Empirical Measure

Let $x = \{x_1, \dots, x_N\}$ be a configuration of points in Λ_N, identified with its cloud $\sum_{i=1}^N \delta_{x_i}$. It decomposes into its connected components

$$[x_i] := \sum_{j \in \Theta_i} \delta_{x_j},$$

Main object: the empirical measure on the connected components, translated such that any of its points is at the origin with equal measure:

$$Y_N^{(x)} = \frac{1}{N} \sum_{i=1}^N \delta_{[x_i]-x_i}.$$

Then the energy is written

$$V_N(x) = \sum_{\substack{i,j=1 \\ i \neq j}}^N v\big(|x_i - x_j|\big) = \sum_{i=1}^N \sum_{\substack{j \neq i \\ x_j \in [x_i]}} v\big(|x_i - x_j|\big) = \sum_{i=1}^N \frac{1}{\#[x_i]} \sum_{\substack{x,y \in [x_i] \\ x \neq y}} v(|x-y|)$$

$$= N\,\Psi\big(Y_N^{(x)}\big),$$

where

$$\Psi(Y) = \int Y(\mathrm{d}A)\, \frac{1}{\#A} \sum_{\substack{x,y \in A \\ x \neq y}} v(|x-y|).$$

On the Proof: Large-Deviation Principle

Let X be a vector of i.i.d. random variables $X_1^{(N)}, X_2^{(N)}, \dots, X_N^{(N)}$ uniformly distributed on Λ_N, and write $Y_N = Y_N^{(X)}$. Hence,

$$Z_N(\beta_N, \rho_N) = \frac{|\Lambda_N|^N}{N!} \mathbb{E}_{\Lambda_N}\Big[\exp\big\{-\beta_N \Psi(Y_N)\big\}\Big].$$

Proposition. $(Y_N)_{N\in\mathbb{N}}$ satisfies a large-deviation principle with speed $N\beta_N$ and rate function

$$J(Y) = c\Big[1 - \int Y(\mathrm{d}A)\,\frac{1}{\#A}\Big].$$

That is,

$$\frac{1}{N\beta_N} \log \mathbb{P}_{\Lambda_N}\big(Y_N \in \cdot\big) \Longrightarrow -\inf_{Y\in\cdot} J(Y).$$

Informally, Varadhan's lemma implies

$$\lim_{N\to\infty} \frac{1}{N\beta_N} \log \mathbb{E}_{\Lambda_N}\Big[\exp\big\{-\beta_N \Psi(Y_N)\big\}\Big] = -\inf_{Y}\big\{\Psi(Y) + J(Y)\big\}.$$

It is not difficult to see that this is basically the assertion.