Phase Transitions for Dilute Particle Systems with Lennard-Jones Potential

Wolfgang König

Weierstraß Institute Berlin and Technical University Berlin

joint with Andrea Collevecchio (Venice), Peter Mörters (Bath) and Nadia Sidorova (London)

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Energy

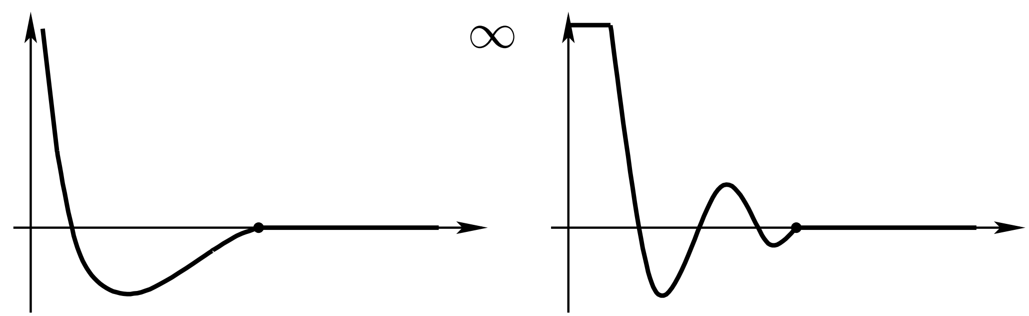
Energy of N particles in $\mathbb{R}^d$:

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

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),
- preference of a certain positive distance,
- bounded interaction length.

Dilute System

Dilute System: N particles in the centred box $\Lambda_N \subset \mathbb{R}^d$ with Volume N^α with $\alpha \in (1,\infty)$.

Partition Function, with a temperature parameter $\beta \in (0,\infty)$,

$$Z_N(\beta) := \frac{1}{|\Lambda_N|^N} \int_{\Lambda_N^N} \mathrm{d}x_1 \ldots \mathrm{d}x_N \ \exp\Big\{ -(\beta \log N) V_N(x_1,\ldots,x_N) \Big\}.$$

Idea: Inverse temperature β_N and particle density ρ_N satisfy

$$\frac{\beta_N}{\log \rho_N} = \frac{\beta}{1-\alpha} = \text{constant.}$$

The log of the entropy is $\log(|\Lambda_N|^N) = O(N \log N)$, the interaction should therefore as well.

Free energy on the scale $N \log N$:

$$\Xi(\alpha,\beta) = \lim_{N\to\infty} \frac{1}{N \log N} \log Z_N(\beta).$$

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

How does the crystalline structure emerge when the temperature is decreased?

Assumptions on the Potential

Assumption (V). $v\colon [0,\infty) \to (-\infty,\infty]$ satisfies

1. There is $\nu_0 \geq 0$ such that $v = \infty$ on $[0,\nu_0]$ and $v < \infty$ on (ν_0,∞);
2. v is continuous on $[0,\infty)$;
3. there is $R > 0$ such that $v = 0$ on $[R,\infty)$;
4. there is $\nu_1 > 0$ such that $v < 0$ on $(R-\nu_1, R)$;
5. there is $\nu_2 > 0$ such that

$$\min_{[0,\nu_2]} v \geq -\nu_2^{-d}(2R)^d \sup_{r\in(0,1]} s(r) r^d \times \min_{[0,\infty)} v.$$

where $s(r)$ denotes the minimal number of balls of radius r in $\mathbb{R}^d$ required to cover a ball of radius one.

In particular,

- v explodes at zero,
- v has a finite and strictly negative minimum,
- the support of v is bounded,
- $0 \leq \nu_0 \leq \nu_2 < R - \nu_1 < R$.

The ground state

Minimal energy of N particles (i.e., '$\beta = \infty$'):

$$\varphi(N) = \inf_{x_1,\dots,x_N \in \mathbb{R}^d} V_N(x_1,\dots,x_N).$$

Lemma.

$$\widetilde{\varphi} = \lim_{N\to\infty} \frac{\varphi(N)}{N} = \inf_{N\in\mathbb{N}} \frac{\varphi(N)}{N} \in (-\infty, 0),$$

- Existence of limit by subadditivity, finiteness by Assumption (V)5., negativity by Assumption (V)4.
- The minimising configurations crystallise, i.e., approach a regular lattice (unique up to shift and rotation) in $d = 1$ [GARDNER/RADIN 1979] and in $d = 2$ [THEIL 2006].

Hence, the following sequence is continuous:

$$\theta_\kappa = \begin{cases} \frac{\varphi(\kappa)}{\kappa}, & \text{if } \kappa \in \mathbb{N}, \\ \widetilde{\varphi}, & \text{if } \kappa = \infty. \end{cases}$$

The Limiting Free Energy

Theorem 1. For any $\alpha \in (1, \infty)$ and any $\beta \in (0, \infty)$,

$$\Xi(\alpha, \beta) = \lim_{N \to \infty} \frac{1}{N \log N} \log Z_N(\beta)$$

exists and is given by

$$\Xi(\alpha, \beta) = 1 - \alpha - \inf \Big\{ \beta \sum_{\kappa \in \mathbb{N} \cup \{\infty\}} q_\kappa \theta_\kappa - (\alpha - 1) \sum_{\kappa \in \mathbb{N}} \frac{q_\kappa}{\kappa} : q \in [0, 1]^{\mathbb{N} \cup \{\infty\}}, \sum_{\kappa \in \mathbb{N} \cup \{\infty\}} q_\kappa = 1 \Big\}.$$

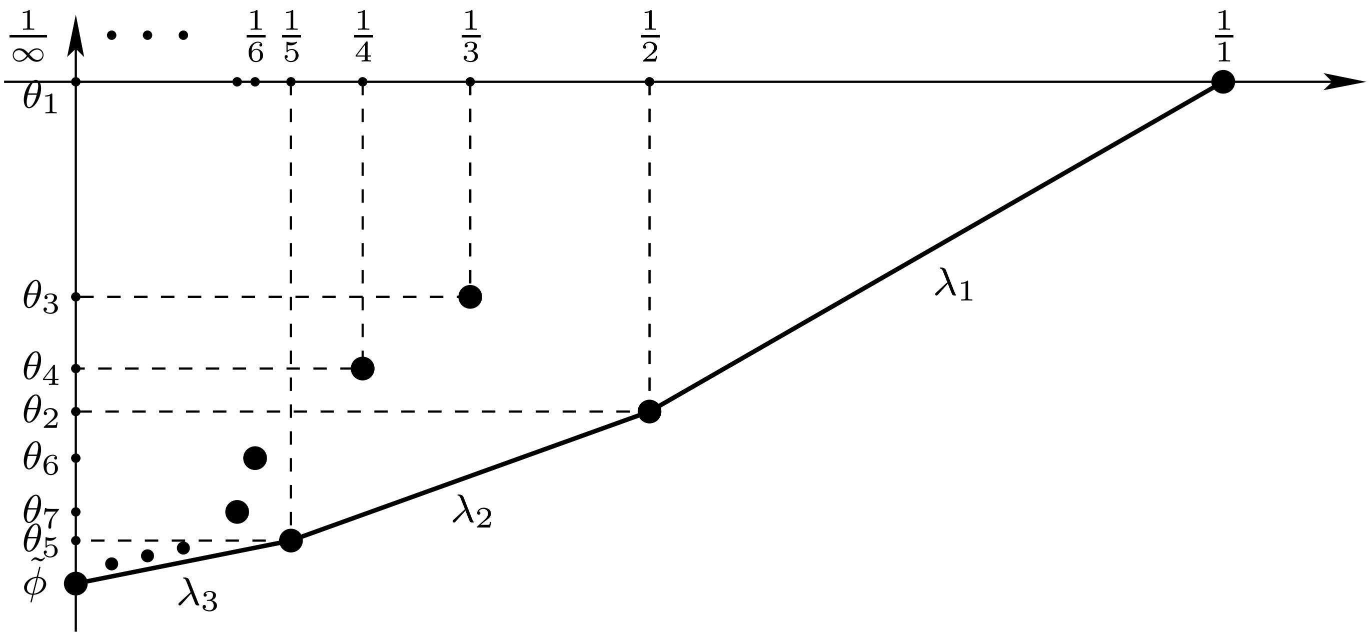
- $-\frac{1}{\beta} \Xi(\alpha, \beta)$ is the free energy per particle.
- In the case of positive particle density (i.e., $\alpha = 1$) at fixed positive temperature (i.e., β instead of $\beta \log N$), the existence of the free energy per particle and of a phase transition is a classical fact [RUELLE 1999, Theorem 3.4.4].

Interpretation of the Formula

- Recall that the support of v is bounded by R. Hence, any point configuration $\{x_1, \dots, x_N\}$ decomposes into R-connected components.
- q_κ is the relative frequency of the components of cardinality κ. More precisely: a given particle belongs with probability q_κ to a component with κ elements.
- That is, $\{x_1, \dots, x_N\}$ consists of Nq_κ/κ components of cardinality κ for each $\kappa \in \mathbb{N}$ (with a suitable adjustment for $\kappa = \infty$).
- Each component of cardinality κ is chosen optimally, i.e., as a minimiser in the definition of $\varphi(\kappa)$.
- $\sum_{\kappa \in \mathbb{N} \cup \{\infty\}} q_\kappa \theta_\kappa$ is the energy coming from such a configuration.
- $1 - \alpha + (\alpha - 1) \sum_{\kappa \in \mathbb{N}} q_\kappa/\kappa$ is the entropy of the configuration (explanation follows).
- Neither information about the locations of the components relative to each other, nor about their shape is present.

Analysis of the Formula

Consider the sequence of points $(1/\kappa, \theta_\kappa)$, $\kappa \in \mathbb{N} \cup \{\infty\}$, and extend them to the graph of a piecewise linear function $[0,1] \to (-\infty, 0]$. Pick those of them which determine the largest convex minorant of this function, $1 = \kappa_1 < \kappa_2 < \dots$:



Put $\eta = \max\{n \in \mathbb{N} \colon \kappa_n < \infty\} \in \mathbb{N} \cup \{\infty\}$ and

$$\lambda_n = \frac{\theta_{\kappa_n} - \theta_{\kappa_{n+1}}}{1/\kappa_n - 1/\kappa_{n+1}} \qquad \text{and} \qquad \beta_n = \frac{\alpha - 1}{\lambda_n}, \quad \text{for } 1 \le n < \eta + 1$$

Notation: $\mathfrak{q}^{(\kappa)} = (\delta_{\kappa,n})_{n \in \mathbb{N} \cup \{\infty\}} = \kappa$-th unit sequence.

The Phase Transitions

Theorem 2.

(i) The sequence $(\beta_n)_{1\le n<\eta+1}$ is positive, finite and strictly increasing.

(ii)

$$\Xi(\alpha,\beta)=\begin{cases}0, & \text{if } \beta\in(0,\beta_1),\\ -\beta\frac{\varphi(\kappa_n)}{\kappa_n}+\frac{\alpha-1}{\kappa_n}+1-\alpha & \text{if } \beta\in[\beta_{n-1},\beta_n) \text{ for some } 2\le n<\eta+1,\\ -\beta\widetilde{\varphi}+1-\alpha & \text{if } \beta\in[\beta_\eta,\infty).\end{cases}$$

(iii) For $\beta\in(0,\infty)\setminus\{\beta_n\colon 1\le n<\eta+1\}$ the minimiser q is unique:

- for $\beta\in(0,\beta_1)$ it is equal to $\mathfrak{q}^{(\kappa_1)}=\mathfrak{q}^{(1)}$,
- for $\beta\in(\beta_{n-1},\beta_n)$, with some $2\le n<\eta+1$, it is equal to $\mathfrak{q}^{(\kappa_n)}$,
- for $\beta=\beta_\infty$ it is equal to $\mathfrak{q}^{(\infty)}$ (this is only applicable if $\eta=\infty$ and $\beta_\infty<\infty$),
- for $\beta\in(\beta_\eta,\infty)$ it is equal to $\mathfrak{q}^{(\infty)}$.

(iv) If $\beta=\beta_n$ for some $1\le n<\eta+1$, then the set of the minimisers is the set of convex combinations of certain $\mathfrak{q}^{(i)}$'s.

- $\eta\ge 1$ is the number of phase transitions. At least the high-temperature phase ($0<\beta\ll 1$) is non-empty, where the point configuration is totally disconnected.
- The low-temperature phase $\beta\gg 1$ is empty if $\eta=\infty$ and $\beta_\eta=\infty$.

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,

$$Z_N(\beta) = \mathbb{E}_{\Lambda_N}\Big[\exp\big\{-(\beta N \log N)\Psi(Y_N)\big\}\Big].$$

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

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

That is,

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

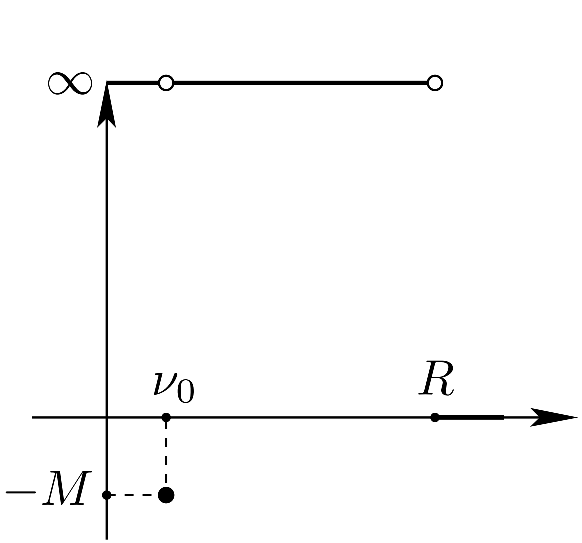
Informally, Varadhan's lemma implies

$$\lim_{N\to\infty} \frac{1}{N\log N}\,\log Z_N(\beta) = -\inf_Y \big\{\beta\Psi(Y) + J(Y)\big\}\,.$$

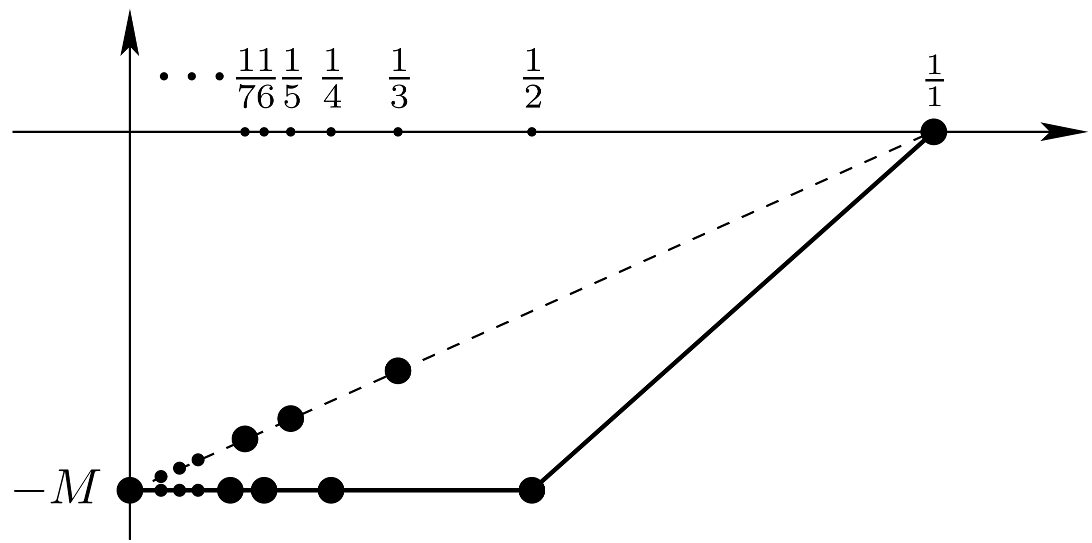
It is not difficult to see that this is basically Theorem 1.

Example: More than one transition

A one-dimensional example of a potential with $\eta \geq 2$, i.e., at least two phase transitions:



Potential v



Phase transitions diagram

(Satisfies Assumption (V) 1.-5. with the exception of 4. A regularized version also satisfies 4.)

Open Questions

- Analyse the precise size of the unbounded component(s).
- Does an unbounded support of v change anything?
- Add kinetic energy, i.e., consider the trace of $\exp\{-(\beta \log N)\mathcal{H}_N\}$, where

$$\mathcal{H}_N = -\sum_{i=1}^{N} \Delta_i + \sum_{1\le i<j\le N} v(|x_i - x_j|).$$

- Other choices of β_N and ρ_N satisfying $\beta_N / \log \rho_N =$ constant.
- Non-dilute systems, i.e., $\alpha = 1$.
- Dilute, but fixed temperature.