Weierstrass Institute for
Applied Analysis and Stochastics

Leibniz Gemeinschaft

Phase Transitions for Dilute Particle Systems with Lennard-Jones Potential

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supported by the DFG-Forschergruppe 718 ‘Analysis and Stochastics in Complex Physical Systems’

Background

Objective: study the transition between gaseous and solid phase in the thermodynamic limit for interacting many-particle systems.

Very difficult at positive temperature and positive particle density. We study a dilute system at vanishing temperature.

Extreme temperature choices:

- fixed positive temperature (inter-particle distance diverges, no interaction felt)
- zero temperature (rigid macroscopic structure emerges).

We study the transition between these two situations.

Questions:

- What is the critical scale?
- What is the emerging microscopical structure?
- What is the emerging macroscopical structure?

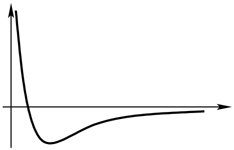
We consider a non-collapsing dilute classical particle system with stable interaction.

Energy

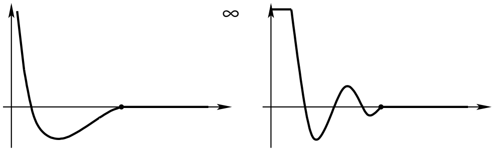
Energy of N particles in $\mathbb{R}^d$:

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

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

N particles in the centred box $\Lambda_N \subset \mathbb{R}^d$ with Volume $|\Lambda_N| \gg N$, i.e., vanishing particle density $\rho_N = N/|\Lambda_N|$.

Partition function with inverse temperature $\beta \in (0,\infty)$,

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

Idea: Couple inverse temperature $\beta = \beta_N \to \infty$ with particle density $\rho_N \to 0$ such that

$$\frac{1}{\beta_N}\log\frac{1}{\rho_N} = c \in (0,\infty) \qquad \text{is constant.}$$

Then energic and entropic forces compete on the same, critical scale, and determine the behaviour of the system. (Example: $\beta_N \asymp \log N$ and $|\Lambda_N| = N^\alpha$ with $\alpha > 1$.)

Free energy per particle:

$$-\Xi(c) = \lim_{N\to\infty} \frac{1}{N\beta_N}\log Z_N(\beta_N,\rho_N).$$

Large $c \Longrightarrow$ entropy wins, i.e., typical inter-particle distance diverges,
Small $c \Longrightarrow$ 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 $v_0 \geq 0$ such that $v = \infty$ on $[0, v_0]$ and $v < \infty$ on (v_0, ∞);
2. v is continuous on $[0,\infty)$;
3. there is $R > 0$ such that $v = 0$ on $[R, \infty)$;
4. there is $v_1 > 0$ such that $v < 0$ on $(R - v_1, R)$;
5. there is $v_2 > 0$ such that

$$\min_{[0,v_2]} v \geq -v_2^{-d}(2R)^d \sup_{r\in(0,1]} s(r) r^d \times \min_{[0,\infty)} v.$$

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,
- $0 \leq v_0 \leq v_2 < R - v_1 < R$.

(i.e., zero temperature):

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

Lemma. [STABILITY OF THE POTENTIAL]

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

- 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. Fix $c \in (0,\infty)$, then for any $\beta_n \to \infty$,

$$-\Xi(c) = \lim_{N\to\infty} \frac{1}{N\beta_N} \log Z_N(\beta_N, \mathrm{e}^{-c\beta_N})$$

exists and is given by

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

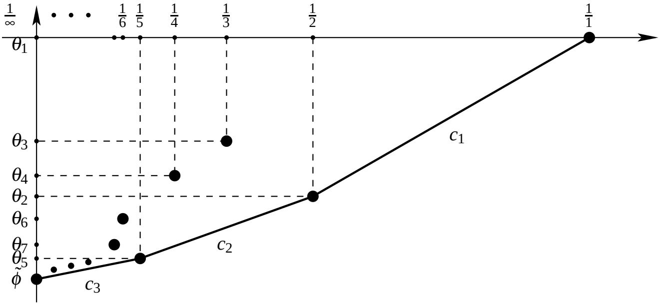
- $-\Xi(c)$ is the free energy per particle.
- In the case of fixed positive particle density at fixed positive temperature, the existence of the free energy per particle and of a close-packing phase transition are classical facts [RUELLE 1999, Theorem 3.4.4].

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.
- $c \sum_{\kappa \in \mathbb{N}} q_\kappa / \kappa$ 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

$$c_n = \frac{\theta_{\kappa_n} - \theta_{\kappa_{n+1}}}{1/\kappa_n - 1/\kappa_{n+1}}, \quad \text{for } 1 \le n < \eta + 1$$

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

Theorem 2.

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

(ii)

$$\Xi(c) = \begin{cases} -c, & \text{if } c\in(c_1,\infty), \\ \frac{\varphi(\kappa_n)}{\kappa_n} - \frac{c}{\kappa_n} & \text{if } c\in[c_n,c_{n-1}) \text{ for some } 2\le n<\eta+1, \\ \widetilde{\varphi} & \text{if } c\in[0,c_\eta). \end{cases}$$

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

- for $c\in(c_1,\infty)$ it is equal to $\mathfrak{q}^{(\kappa_1)} = \mathfrak{q}^{(1)}$,
- for $c\in(c_n,c_{n-1})$, with some $2\le n<\eta+1$, it is equal to $\mathfrak{q}^{(\kappa_n)}$,
- for $c=c_\infty$ it is equal to $\mathfrak{q}^{(\infty)}$ (this is only applicable if $\eta=\infty$ and $c_\infty>0$),
- for $c\in(0,c_\eta)$ it is equal to $\mathfrak{q}^{(\infty)}$.

(iv) If $c=c_n$ 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 ($1\ll c<\infty$) is non-empty, where the point configuration is totally disconnected.
- The low-temperature phase $c\ll 1$ is empty if $\eta=\infty$ and $c_\eta=0$.

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,

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

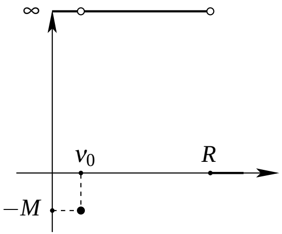
Informally, Varadhan's lemma implies

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

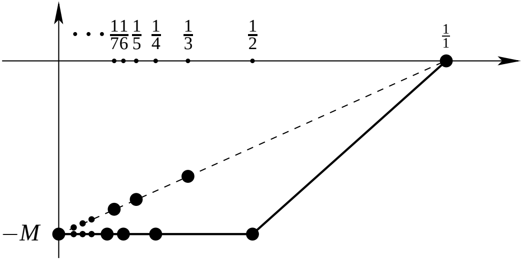
It is not difficult to see that this is basically Theorem 1.

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 $\exp\{-\beta_N \mathscr{H}_N\}$, where

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

- Non-dilute systems.