Phase Transitions for Dilute Particle Systems with Lennard-Jones Potential

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Energy

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

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

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

Lennard-Jones potential

\[ v(r) = r^{-12} - r^{-6} \]

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

examples of our potentials
Dilute System

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

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

\[ Z_N(\beta) := \frac{1}{|\Lambda_N|^N} \int_{\Lambda_N^N} dx_1 \ldots dx_N \exp \left\{ - (\beta \log N)V_N(x_1, \ldots, x_N) \right\}. \]

Idea: Inverse temperature $\beta_N$ and particle density $\rho_N$ 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 $\beta \implies$ entropy wins, i.e., typical inter-particle distance diverges,

Large $\beta \implies$ 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). \( v: [0, \infty) \to (-\infty, \infty] \) satisfies

1. There is \( \nu_0 \geq 0 \) such that \( v = \infty \) on \([0, \nu_0]\) and \( v < \infty \) on \((\nu_0, \infty)\);
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., ‘\( \beta = \infty \)’):

\[
\varphi(N) = \inf_{x_1, \ldots, x_N \in \mathbb{R}^d} V_N(x_1, \ldots, x_N).
\]

**Lemma.**

\[
\tilde{\varphi} = \lim_{N \to \infty} \frac{\varphi(N)}{N} = \inf_{N \in \mathbb{N}} \frac{\varphi(N)}{N} \in (-\infty, 0),
\]

- **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:

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

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

$-\frac{1}{\beta} \Xi(\alpha, \beta)$ is the free energy per particle.

In the case of positive particle density (i.e., $\alpha = 1$) at fixed positive temperature (i.e., $\beta$ 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 $\{x_1, \ldots, x_N\}$ decomposes into $R$-connected components.

- $q_\kappa$ is the relative frequency of the components of cardinality $\kappa$. More precisely: a given particle belongs with probability $q_\kappa$ to a component with $\kappa$ elements.

- That is, $\{x_1, \ldots, x_N\}$ consists of $Nq_\kappa/\kappa$ components of cardinality $\kappa$ for each $\kappa \in \mathbb{N}$ (with a suitable adjustment for $\kappa = \infty$).

- Each component of cardinality $\kappa$ 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.
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 \([0, 1] \rightarrow (-\infty, 0]\). Pick those of them which determine the largest convex minorant of this function, \(1 = \kappa_1 < \kappa_2 < \ldots\):

\[
\begin{align*}
\frac{1}{\infty} &\quad \cdots \quad \frac{1}{6} \quad \frac{1}{5} \quad \frac{1}{4} \quad \frac{1}{3} \quad \frac{1}{2} \quad \frac{1}{1} \\
\theta_1 &\quad \theta_2 &\quad \theta_3 &\quad \theta_4 &\quad \theta_5 &\quad \theta_6 &\quad \theta_7 \\
\lambda_1 &\quad \lambda_2 &\quad \lambda_3 \\
&\quad \phi
\end{align*}
\]

Put \(\eta = \max\{n \in \mathbb{N} : \kappa_n < \infty\} \in \mathbb{N} \cup \{\infty\}\) and

\[
\lambda_n = \frac{\theta_{\kappa_n} - \theta_{\kappa_{n+1}}}{1/\kappa_n - 1/\kappa_{n+1}} \quad \text{and} \quad \beta_n = \frac{\alpha - 1}{\lambda_n}, \quad \text{for} \ 1 \leq n < \eta + 1
\]

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

Theorem 2.

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

(ii) 

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

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

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

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

\(\eta \geq 1\) 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.

\(\beta \gg 1\) 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 \(\beta_\eta = \infty\).

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Let $x = \{x_1, \ldots, x_N\}$ be a configuration of points in $\Lambda_N$, 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:

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

Then the energy is written

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

$$= N \Psi(Y^{(x)}_N),$$

where

$$\Psi(Y) = \int Y(dA) \frac{1}{\#A} \sum_{x \neq y \atop x \neq y} v(|x - y|).$$
Let $X$ be a vector of i.i.d. random variables $X_1^{(N)}, X_2^{(N)}, \ldots, X_N^{(N)}$ uniformly distributed on $\Lambda_N$, and write $Y_N = Y_N^{(X)}$. Hence,

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

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

$$J(Y) = (\alpha - 1) \left[ 1 - \int Y(dA) \frac{1}{\#A} \right].$$

That is,

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

Informally, Varadhan's lemma implies

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

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:

(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

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

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