Some surprises in lattice problems

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Experimental Mathematics Seminar
Rutgers University
April 17, 2025
Minor editions after the talk, on April 18
Additions after the talk, on April 19

Lennard-Jones crystals 101

"On April 22, 1924, the Royal Society of London received a paper written by a research student at Trinity College at Cambridge, John Edward Jones, ..."

"In Lennard-Jones' third paper of 1924, lattice sums were introduced to obtain bulk properties for cubic crystals. This work is particularly interesting (and perhaps less well-known to the chemistry community), as it opened up a whole new field in mathematical lattice theory."

Quoted from:

100 Years of the Lennard-Jones potential
Peter Schwerdtfeger and David J. Wales
J. Chem. Theory and Comp. **20**, 3379–3405 (2024).

The family of Lennard-Jones potentials

In his first article of 1924, (then still) Jones proposed that the potential energy $V(r)$ of two like atoms a distance $r > 0$ apart (measured center to center) is given by

$$V_{n,m}(r) := \frac{A_n}{r^n} - \frac{B_m}{r^m}; \quad n > m > 0,$$

where $A_n > 0$ and $B_m > 0$ are two constants that need to be matched to the species of atoms under consideration.

This potential pair energy had actually been proposed earlier, in 1912, by **Eduard Grüneisen**, who was inspired by even earlier work of **Gustav Mie** from (1903), who proposed the same pair energy though with $n = 5$.

However, these earlier proposals were made in the context of solid state physics, and the theoretical physics community did not have much overlap with the theoretical chemistry community (still true nowadays).

THE Lennard-Jones potential

Using either updated Newtonian mechanics or quantum mechanics, one concludes that $m = 6$ for neutral, though polarizable atoms.

For mathematical convenience (employing the “quadratic formula”) one then chooses $n = 12$. Thus, after suitable scaling, one considers

$$V_{\rm LJ}(r) := 4\varepsilon \left(\frac{\sigma^{12}}{r^{12}} - \frac{\sigma^6}{r^6} \right).$$

Here, σ is a reference length, and ε a reference energy. We will choose $\sigma = 1$ and $\varepsilon = \frac{1}{4}$.

3-dimensional crystals

100 years ago, in 1925, (then still) Jones, jointly with Albert Ingham, published the paper titled:

“On the calculation of certain crystal potential constants, and on the cubic **crystal of least potential energy**”

They concluded that among the standard cubic lattices (fcc, bcc, simple cubic) the fcc lattice has the lowest energy per particle. Much later (2023) it was proved by Bétermin and Šamaj that the hcp packing has lower energy per particle.

In any event, the Jones & Ingham paper became the template for computing crystal structures that “match” those seen in nature. We illustrate how this is done using a 1D toy model.

1-dimensional illustration

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$$W(a) = \sum_{k\in\mathbb{Z}\setminus\{0\}} V_{\mathrm{LJ}}(|ka|)$$

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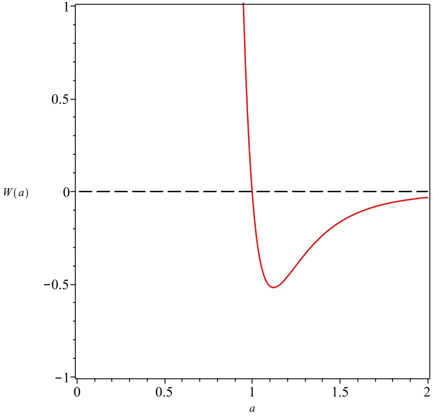
- Since $\sum_{\ell\in\mathbb{N}} \frac{1}{\ell^c}$ converges when $c > 1$, we obtain

$$W(a) = \sum_{k\in\mathbb{Z}\setminus\{0\}} \frac{1}{(ak)^{12}} - \sum_{k\in\mathbb{Z}\setminus\{0\}} \frac{1}{(ak)^{6}} = \frac{2\zeta(12)}{a^{12}} - \frac{2\zeta(6)}{a^{6}}.$$

The LJ potential energy per particle



Lennard-Jones energy per particle as function of lattice spacing a

Manifestly there exists a unique minimum at some a_{min}, easily determined via calculus to be at $a_{\text{min}} = (2\zeta(12)/\zeta(6))^{\frac{1}{6}}$.

Choosing $a = a_{\text{min}}$ gives the ∞ long idealization of an LJ crystal in a hypothetical 1D world.

Why minimizing energy gives the right physics?

The **usual narrative** is that without kinetic energy in the system (N.B.: we are neglecting the influence of temperature, which would cause the atoms to jiggle around their equilibrium positions), the stable crystal state is attained when each atom is in its lowest energy state, and minimizing w.r.t. a gives you that.

But why that narrative?

Answer: Empirical observations show that if you slowly cool down a liquid (like liquid water) it will eventually crystalize into solid water ice, having lower energy than the same amount of liquid water at higher temperature. Our physical theories are designed to reflect those observations in the mathematics of our idealized models of nature.

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$$F_{\text{LJ}}(x|y) = -\frac{\partial}{\partial x} V_{\text{LJ}}(|x - y|),$$

and this also obeys Newton’s “**actio** $=$ **re-actio**,” viz.

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- Newton’s EoM:

$$\forall i \in \mathbb{Z}: \qquad \frac{d^2}{dt^2} x_i(t) = \sum_{j \neq i} F_{\text{LJ}}\big(x_i(t)|x_j(t)\big).$$

Dilational Dynamics

The oscillatory motions of perturbed lattices can be very complicated. So let’s look at the simplest special case that comes to mind:

- Imagine the ∞ LJ chain to be either **compressed** or **stretched** *uniformly* away from its equilibrium state, and then released from such a constrained initial state, evolving henceforth as per Newton’s equations of motion.

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- The keyword is "uniformly;" so we cleverly anticipate the final result of a lengthy calculation, the *effective differential equation* for the lattice spacing $a(t)$ as function of time, viz.

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- **Initial data**: $a(0) = a_0$ and $\frac{d}{dt}a(t)|_{t=0} = 0$.

Dilational Dynamics (cont.^{d})

This one-dimensional effective dynamical equation for $a(t)$ is solvable in closed form, though not necessarily explicitly for a as function of t, but for t as function of a, using the so-called *energy method*.

The energy method yields (for sufficiently short times)

$$t(a) = \pm \int_{a_0}^{a} \frac{dr}{\sqrt{2\Big(W(a_0) - W(r)\Big)}},$$

where "$+$" is to be used for a compressed initial state,
"$-$" for the stretched one.

N.B.: This method yields a patchwork job (turning point to turning point, repeat); in the small-amplitude approximation one gets $a(t) - a_{\min} = \big(a_0 - a_{\min}\big)\cos(\omega t)$ for some $\omega > 0$.

Dilational Dynamics (cont.^{d})

BUT: Let’s check whether this “ingenious” guess is correct!

- We evaluate the total Newtonian force acting on any particular point particle in the stipulated initial state of the chain of evenly spaced ∞ many Lennard-Jones atoms with nearest neighbor spacing $a \neq a_{\rm min}$.

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- Now we notice that, for each $i \in \mathbb{Z}$ and $k \in \mathbb{N}$,

$$F_{\text{LJ}}(x_i|x_i + ka) = -F_{\text{LJ}}(x_i|x_i - ka),$$

and so, initially:

$$\sum_{j \neq i} F_{\text{LJ}}\big(x_i|x_j\big) = \sum_{k \in \mathbb{N}} F_{\text{LJ}}\big(x_i|x_i - ka\big) + F_{\text{LJ}}\big(x_i|x_i + ka\big) = 0 \quad (!)$$

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- **UPSHOT**: The chain is in equilibrium for any a !

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- YES! $\forall i \in \mathbb{Z}$, the *series over all LJ forces on particle i* is **absolutely summable**
- **UPSHOT**: The ∞ chain **is** in force equilibrium for any a ! While **counter-intuitive**, it is **true nevertheless**.

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- In the stipulated IVP for the ∞ chain with spacing a, the particles of the chain would not "know" which one should stay put while the others should start to move!

Lowest LJ energy clusters

This is an **NP-hard** problem.

- For $2 \leq N < 2000$ ($\approx$, say) there are computer-generated data available that passed some optimality tests.
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- For N not larger than a few 1000, there are **lots** of structural transitions:
  E.g., Mackay to anti-Mackay icosahedral structure, vs. decahedral structure, etc.
- For N very very large, on the other hand, one can safely assume that the ∞ crystal lattice results show the way toward an asymptotic expansion, at least for the energy.

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- Suppose the Lennard-Jones N body cluster for $N \gg 1$ is $\approx$ polyhedral in shape, then its energy is expected to be

$$\mathcal{E}(N) = \alpha V + \beta A + \gamma E + \delta C + \text{c.a.c} \qquad (*)$$

where V is the volume, A the surface area, E the edge length, and C the number of corners of the polyhedron (e.g. 8 for a cube); the N dependence is $V \propto N$, $A \propto N^{2/3}$, $E \propto N^{1/3}$. The c.a.c are “centered atomic contributions,” less regular, and account for the fact that our perceived continua are actually atomistic in nature.

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- Lattice sum calculations should yield $\alpha, \beta, \gamma, \delta$.

Lowest LJ energy clusters with $n = 2m \to \infty$

When we replace the so-called 12-6 potential by the Grüneisen / general Lennard-Jones n-m potential, with $n = 2m$, and let $m \to \infty$, we obtain the limit of *sticky hard spheres*. The lowest energy is the negative of the largest number of kissing points.

The 2D special case has been solved

The lowest energy as function of N reads (Harborth, 1974):

$$\mathcal{E}(N) = -\lfloor 3N - \sqrt{12N - 3} \rfloor$$

The floor function makes it plain that this is not an analytic expression in $\sqrt{N}$. It produces the “atomic contributions.”

Asymptotics of the Harborth function

We can extract an analog of the asymptotic expansion $(*)$, viz.

$$\mathcal{E}(N) = \alpha A + \beta E + \gamma C + \text{c.a.c.} \qquad (**)$$

where now $A \propto N$, $E \propto N^{\frac{1}{2}}$, $C = 6$. Thus $(**)$ is the same as

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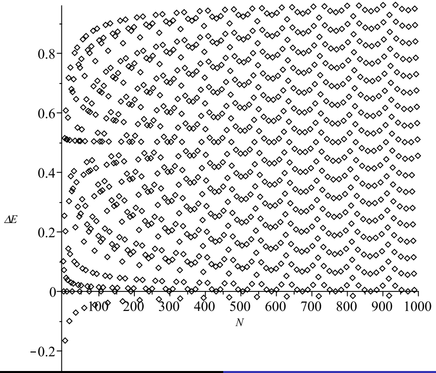
- Already the next term is strongly fluctuating.

Asymptotics of the Harborth function

The figure shows $\Delta E(N) := \mathcal{E}(N) + 3N - 2\sqrt{3}N^{\frac{1}{2}}$ vs. N, where $\mathcal{E}(N)$ is the Harborth function. One can shift ΔE by a constant to center it at zero (asymptotically as $N \sim \infty$), thus obtaining the term γ. Such centered "atomic contributions" account for the microscopic discreteness of our matter in bulk.



That’s it (for now) / MANY THANKS!

There is a surprising regularity embedded in the “irregular” fluctuations.

To be continued ...