Unusual Classical Ground States of Matter

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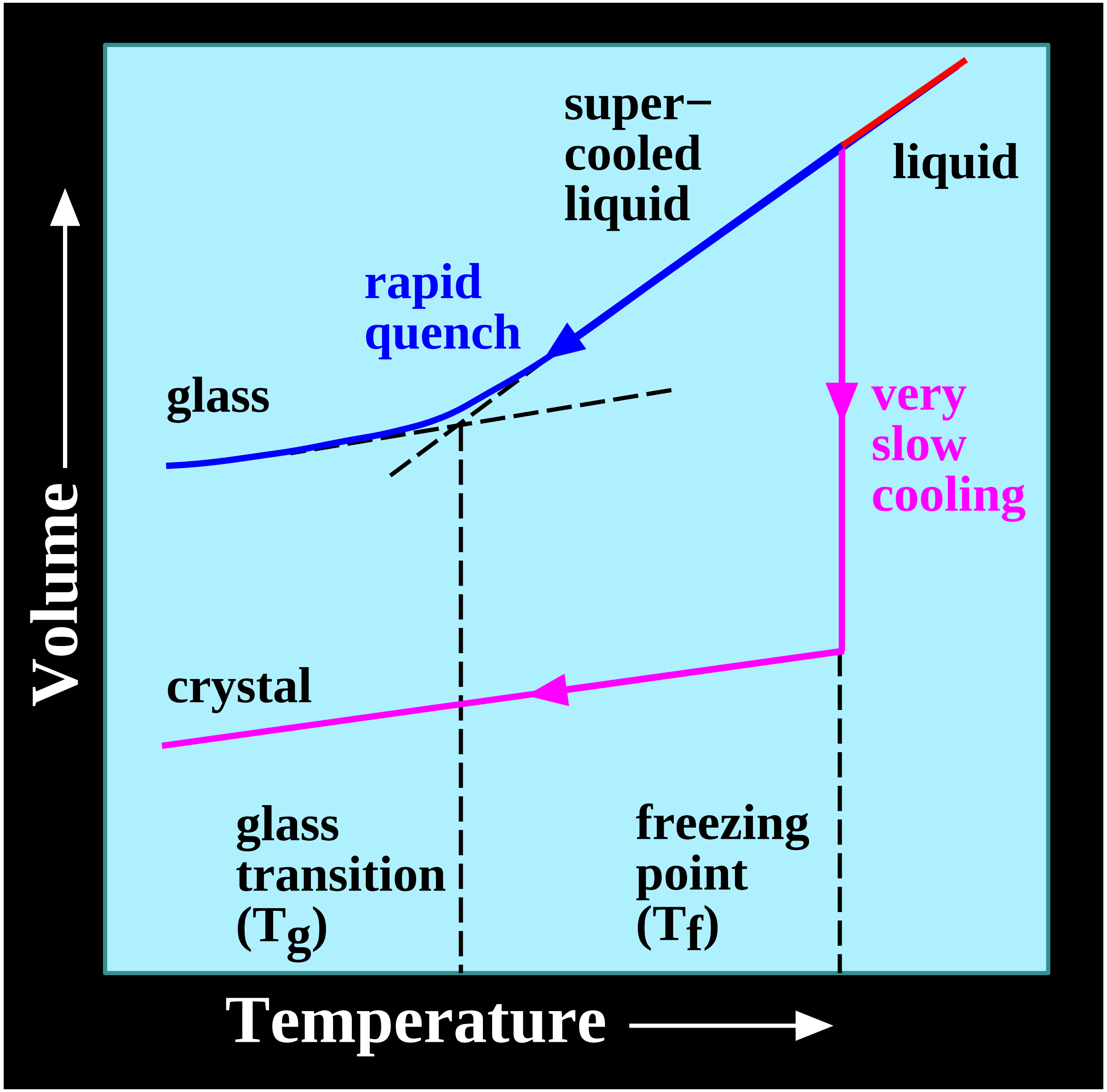
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Classical Ground States

- Classical **ground states** are those classical particle configurations with **minimal** potential energy per particle $\Phi_N(\mathbf{r}^N)/N$.
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- To What Extent Can We Predict/Control Ground-State Structures?
- Can Ground States Ever Be Disordered? There is no fundamental reason why aperiodic or disordered ground states are prohibited in low dimensions (Ruelle 1982).

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• We provide some specific answers to these questions using **optimization techniques**.

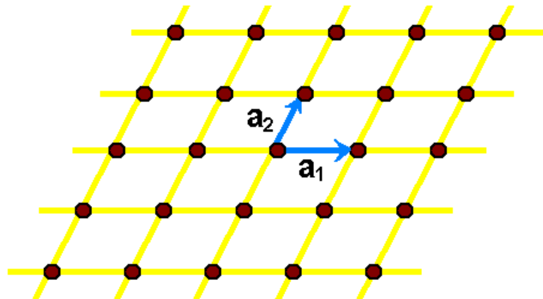
Definitions

- **A lattice in d-dimensional Euclidean space $\mathbb{R}^d$ is the set of points that are integer linear combinations of d basis (linearly independent) vectors, i.e., for basis vectors $\mathbf{a}_1, \ldots, \mathbf{a}_d$,**

$$\{n_1\mathbf{a}_1 + n_2\mathbf{a}_2 + \cdots + n_d\mathbf{a}_d \mid n_1, \ldots, n_d \in Z\}$$

The space $\mathbb{R}^d$ can be geometrically divided into identical regions F called fundamental cells, each of which contains just one point.

In $\mathbb{R}^2$:



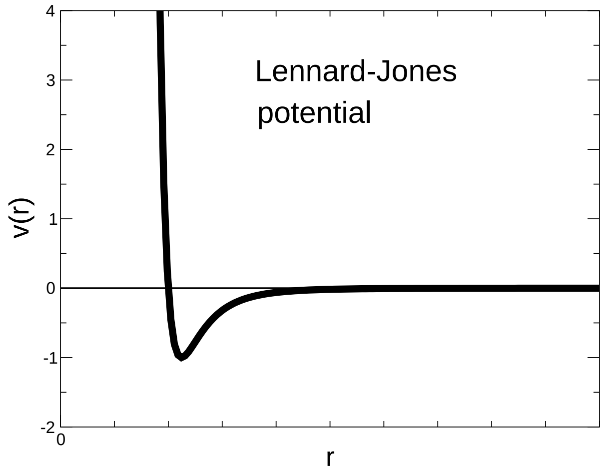
- **A periodic point distribution in $\mathbb{R}^d$ is a fixed configuration of N points (where $N \geq 1$) in each fundamental cell of a lattice.**

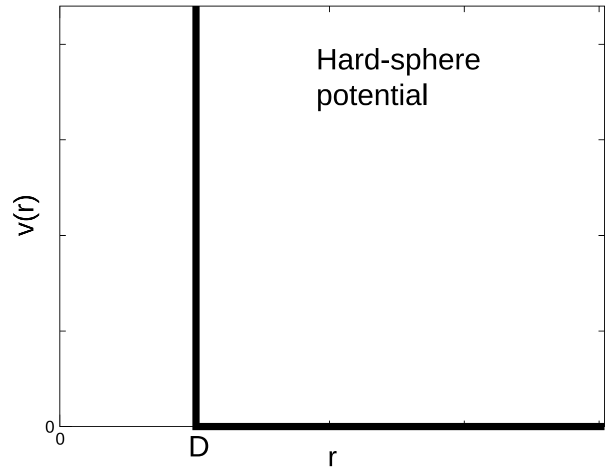
Simple Pair Interactions

- For a configuration $\mathbf{r}^N \equiv \mathbf{r}_1, \ldots, \mathbf{r}_N$ of $N \gg 1$ particles in volume $V \subset \mathbb{R}^d$, the simplest form for the total potential energy is

$$\Phi_N(\mathbf{r}^N) = \sum_{i<j} v(|\mathbf{r}_j - \mathbf{r}_i|),$$

where $v(r)$ is a "stable" radial function.





- Ground state in $\mathbb{R}^3$ of Lennard-Jones (LJ) potential is strongly believed to be one of the stacking variants of the densest sphere packings (Hales 2005), but there is no proof. The unbounded support of the LJ potential makes the problem highly nonlocal.

Local Density Fluctuations for General Point Distributions

Torquato and Stillinger, PRE 68, 041113 (2003)

- **Points can represent molecules of a material, stars in a galaxy, or trees in a forest. Let Ω represent a regular domain (window) in $\mathbb{R}^d$ and $\mathbf{x}_0$ denote its centroidal position.**

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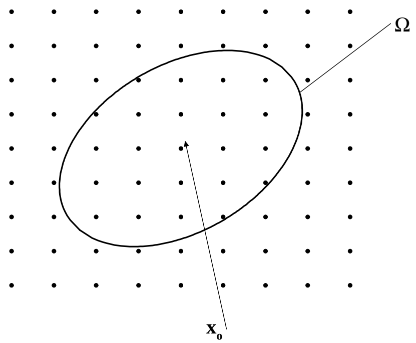

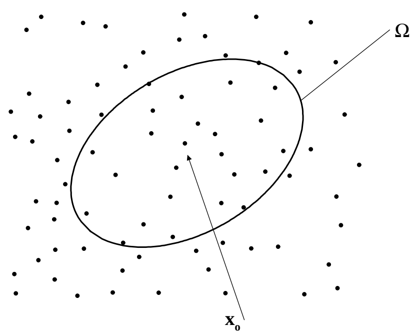

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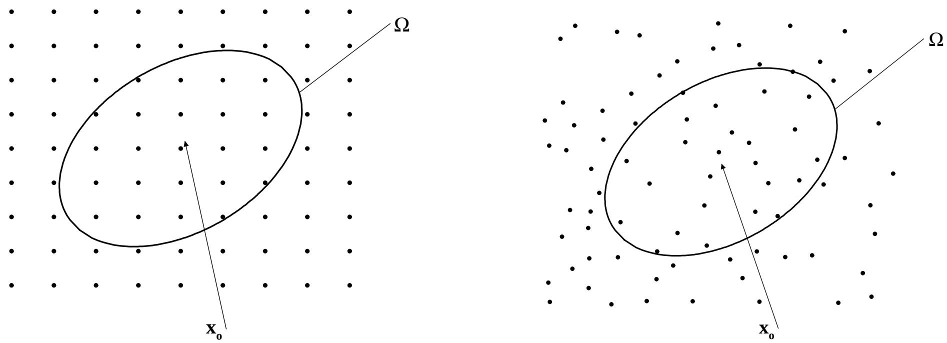


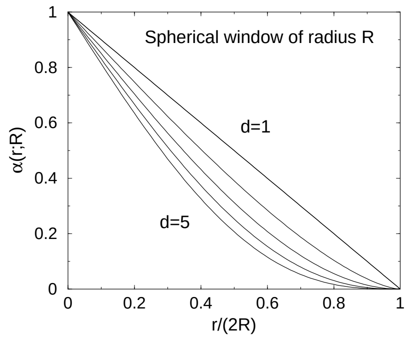
- **For a d-dimensional spherical window of radius R in $\mathbb{R}^d$, denote by $\sigma^2(R) \equiv \langle N^2(R)\rangle - \langle N(R)\rangle^2$ the number variance.**
- **For a Poisson point process and many correlated point distributions, $\sigma^2(R) \sim R^d$.**
- **We call point distributions whose variance grows more slowly than R^d hyperuniform (infinite-wavelength fluctuation vanish).**

SINGLE-CONFIGURATION FORMULATION

- **We showed**

$$\sigma^2(R) = 2^d \phi \left(\frac{R}{D}\right)^d \left[1 - 2^d \phi \left(\frac{R}{D}\right)^d + \frac{1}{N} \sum_{i \neq j}^{N} \alpha(r_{ij}; R)\right]$$

where $\alpha(r;R)$ is scaled intersection volume of 2 windows separated by r, which can be viewed as a repulsive pair potential:



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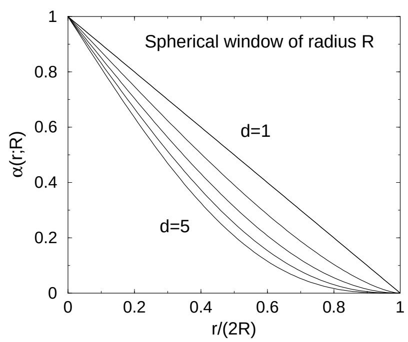

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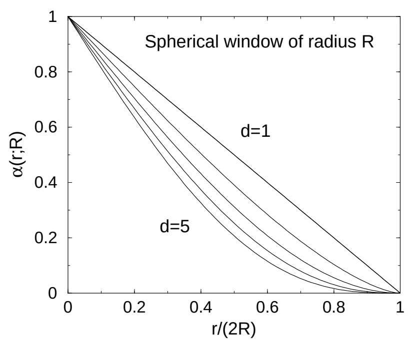

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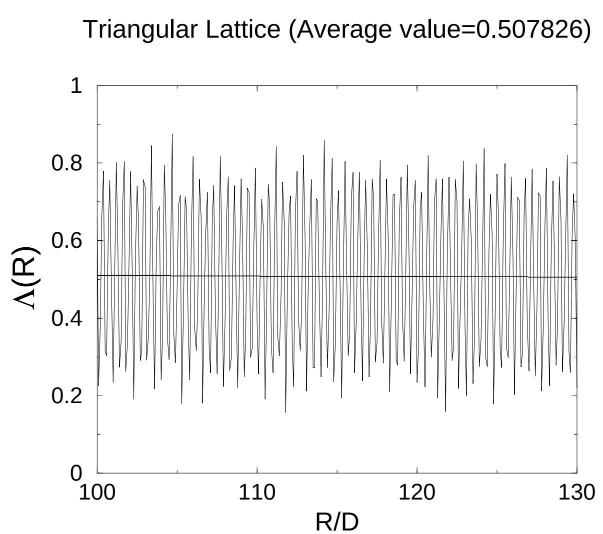

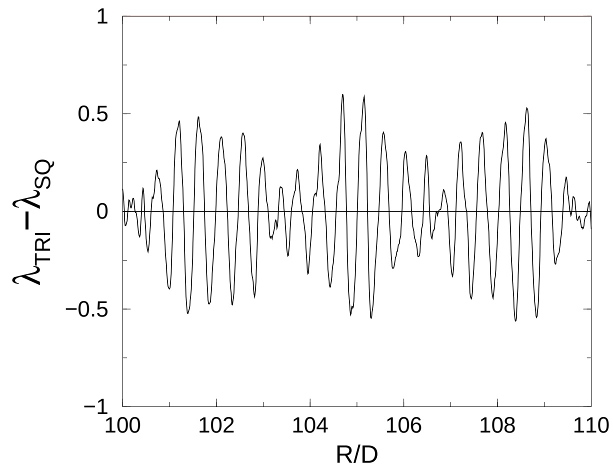

RESULTS FOR BRAVAIS LATTICES & NUMBER THEORY

- **Lattice in $\mathbb{R}^d$ is specified by the primitive lattice vector**

$$\mathbf{p} = n_1\mathbf{a}_1 + n_2\mathbf{a}_2 + \cdots + n_{d-1}\mathbf{a}_{d-1} + n_d\mathbf{a}_d = \mathbf{A}\cdot\mathbf{n}$$

- **Define the positive definite quadratic form in $n_1, n_2, \ldots, n_d$:**

$$Q(\mathbf{n}) = p^2 \equiv \mathbf{p}^T\cdot\mathbf{p} = \mathbf{n}^T\cdot\mathbf{B}\cdot\mathbf{n}, \qquad (\mathbf{B} = \mathbf{A}^T\cdot\mathbf{A})$$

- **$N(\mathbf{x}_0;R)$ is a periodic function in the window position $\mathbf{x}_0$:**

$$N(\mathbf{x}_0;R) = \rho v_1(R) + \sum_{\mathbf{q}\neq\mathbf{0}} a(\mathbf{q})e^{i\mathbf{q}\cdot\mathbf{x}_0} \qquad (\mathbf{q}\cdot\mathbf{p} = 2\pi m)$$

- **We showed that**

$$\sigma^2(R) = \frac{R^d}{v_C^2}\sum_{\mathbf{q}\neq\mathbf{0}}\left(\frac{2\pi}{q}\right)^d [J_{d/2}(qR)]^2, \qquad \overline{\Lambda} = \frac{2^d\pi^{d-1}D^{2d}}{v_C^2}\sum_{\mathbf{q}\neq\mathbf{0}}\frac{1}{(qD)^{d+1}}.$$

- **For $Q(\mathbf{m})$, Epstein zeta function for a lattice is defined by**

$$Z_Q(s) = \sum_{\mathbf{m}\neq\mathbf{0}} Q(\mathbf{m})^{-s}, \qquad \text{Re } s > d/2.$$

Quantifying Degree of Order

- The surface-area coefficient $\overline{\Lambda}$ for some crystal, quasicrystal and disordered two-dimensional hyperuniform point patterns.

Pattern	$\overline{\Lambda}/\phi^{1/2}$
Triangular Lattice	0.508347
Square Lattice	0.516401
Honeycomb Lattice	0.567026
Kagomé Lattice	0.586990
Penrose Tiling	0.597798
Step+Delta-Function g_2	$2^{5/2}/(3\pi) \approx 0.600211$
Step-Function g_2	$8/(3\pi) \approx 0.848826$
One-Component Plasma	$2/\sqrt{\pi} \approx 1.12838$

- We found analogous results in $\mathbb{R}^3$.

Minimum of Epstein Zeta Function in Higher Dimensions

- **Because of the connection with optimal packing problems, Rankin (1953) conjectured and proved that the minimum value of the Epstein zeta function in $\mathbb{R}^2$ at $s = 3/2$ is achieved by the triangular lattice.**

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$$Z_Q(s) \geq Z_{Q_L}(s),$$

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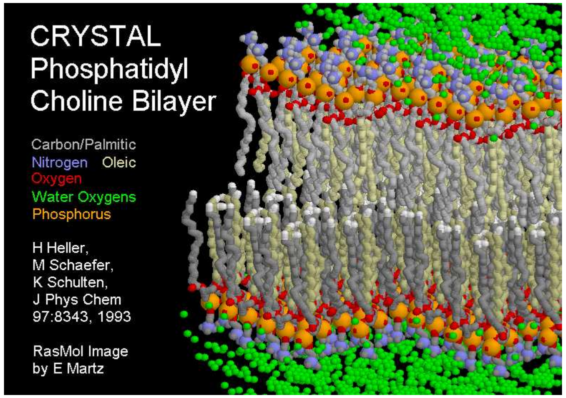
- Whenever the conjecture is true, the number variance is minimized by lattices that are the duals to those that minimize the Epstein zeta function.
- Sarnak and Strömbergsson (2006) have recently proved that the conjecture cannot be generally true, but for $d = 4, 8$ and 24, $Z_{Q_L}(s)$ is locally minimum.

Inverse Problem of Statistical Mechanics

- **Traditional Self Assembly**
  - **"Self-assembly" – processes in which entities (atoms, molecules, aggregates of molecules, etc.) spontaneously arrange themselves into a larger ordered and functioning structure.**
  - **Biology offers wonderful examples: (1) DNA double helix; (2) lipid bilayers; and (3) protein folding.**



  - **Materials science of the future, i.e., devising building blocks with specific interactions that can self-organize on a number of length scales.**
  - **Edisonian approaches. Theory?**

Inverse Approach

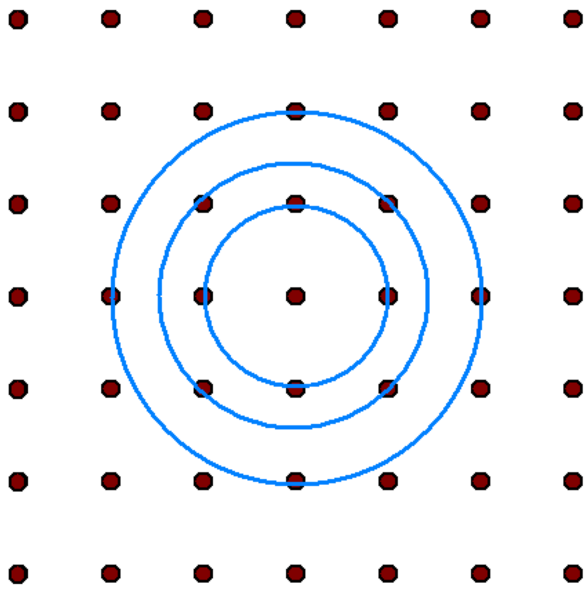
- **Two-fold objective:**
  1. **Statistical-mechanical methodology to find interaction potential in many-body systems that lead spontaneously to a "target" structure.**
  2. **Use this knowledge to create such targeted colloidal structures.**
- **"Inverse" approach holds great promise for controlling self-assembly to a degree that surpasses the less-than-optimal path that nature has provided.**
- **Indeed, can "tailor" potentials that produce varying degrees of disorder, thus extending the traditional idea of self-assembly to incorporate crystal, quasicrystal, and amorphous structures.**

Motivation

- Rich fundamental statistical-mechanical issues and questions offered by this fascinating inverse problem. For example,
  1. A deeper fundamental understanding of the mathematical relationship between the collective behavior of many-body systems and the interactions.
  2. What are the class of structures realizable by spherically symmetric pair potentials and what are its limitations? When is anisotropy in the potential required? When is nonadditivity required?
- Our recent ability to identify target structures that have unique or desirable material properties. For example,
  1. negative thermal expansion or negative Poisson's ratio materials
  2. diamond lattice (photonic materials)
  3. quasicrystals
  4. amorphous structures
  5. hyperuniform systems

Challenges

- Strategically placed **deep potential wells**:



- **Pair-distance distributions are unique among the lattices for the first three space dimensions. This is generally not true for $d \geq 4$.**
- **The pair-distance distribution $g_2(r)$ is generally nonunique for point distributions in any dimension.**
- **A known ground state is generally achieved by an infinite set of pair interactions. How does one choose from this infinte set?**

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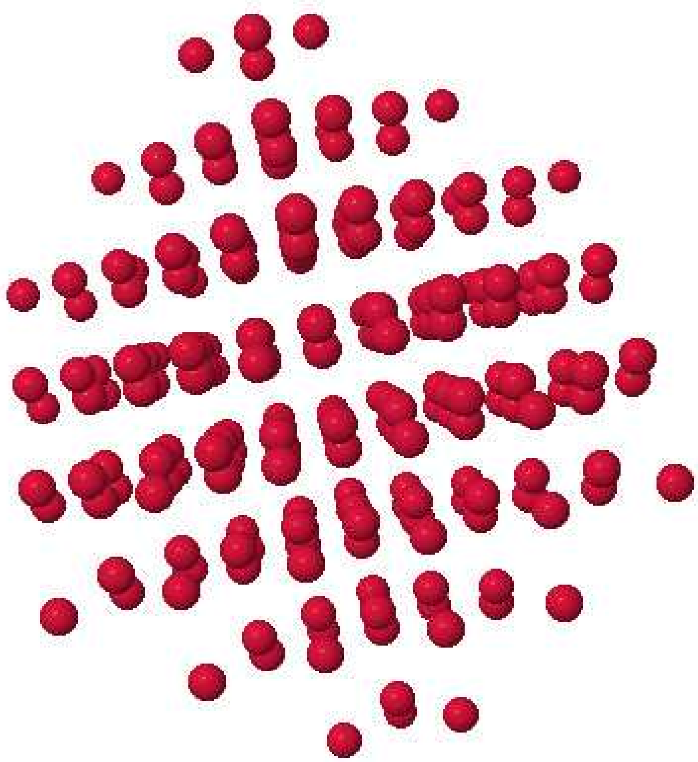
- **Standard short-range interactions often lead to close-packed crystals as ground state.**

Diamond Lattice?



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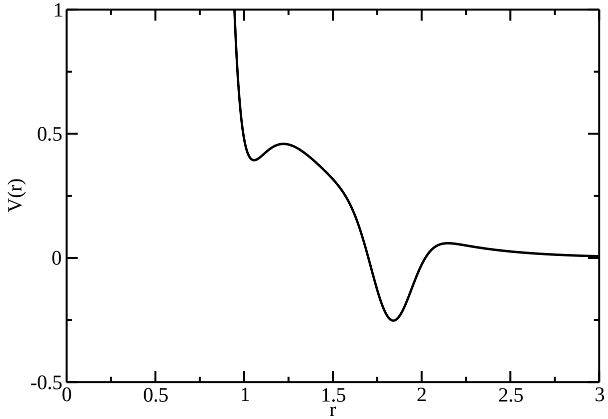

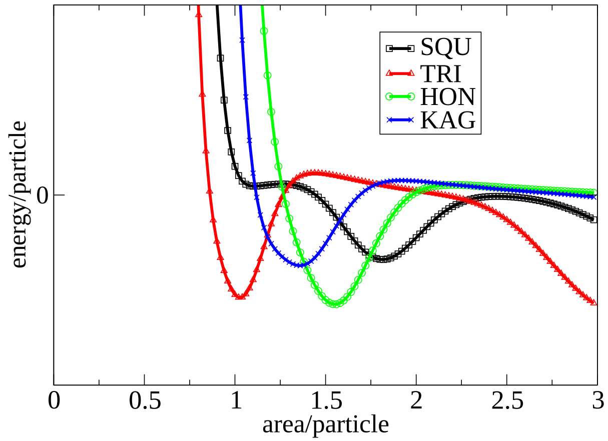

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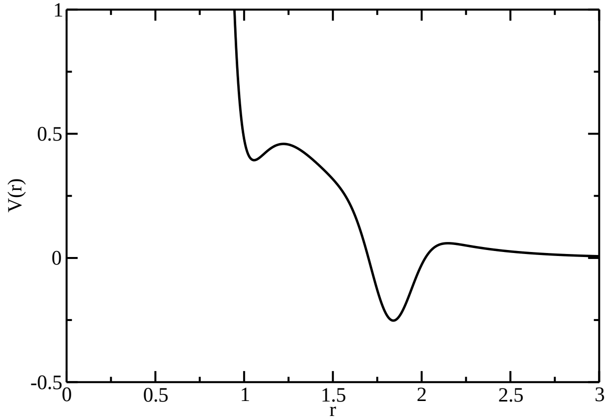
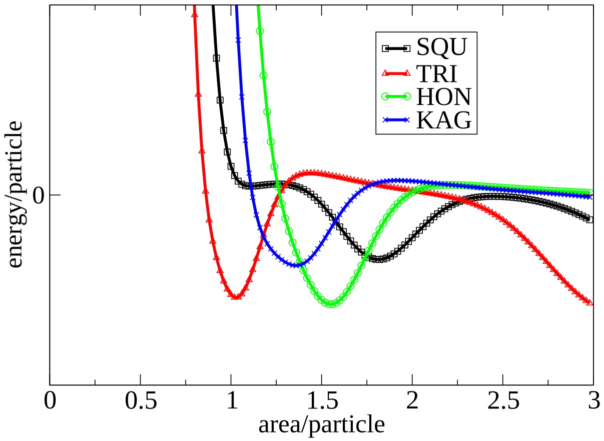
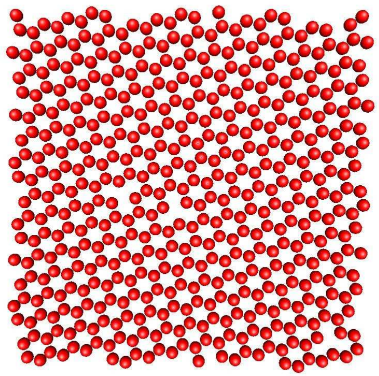




- **Self-assembles in a MD simulation starting above the melting point:**



Rechtsman, Stillinger & Torquato, Physical Review Letters, 2005

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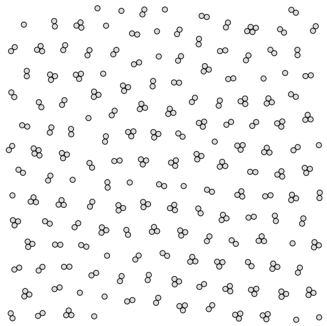

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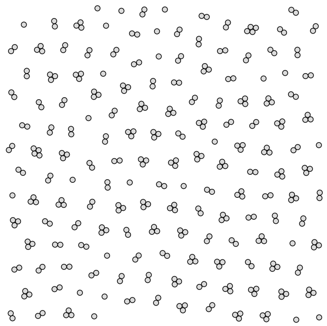

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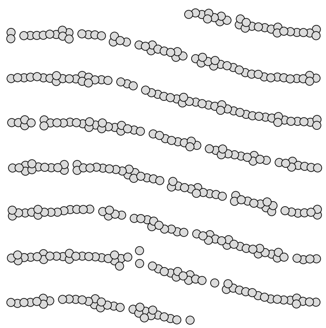

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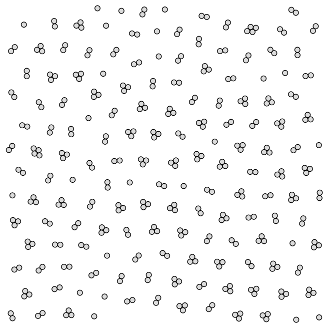

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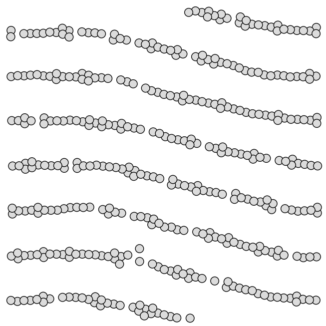

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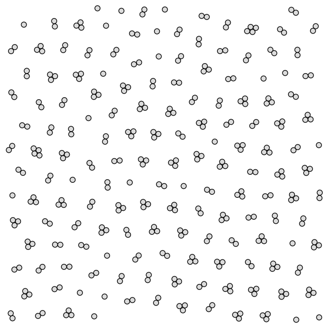

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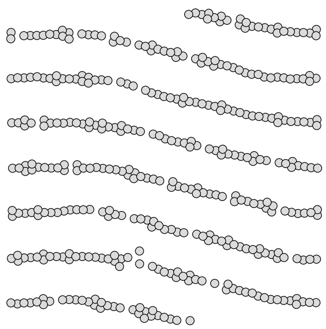

- **Can we produce materials with negative thermal expansion and negative Poisson's ratio?**
- **More recently, investigating soft repulsive (monotonically decreasing) functions.**

Disordered (Highly Irregular) Ground-State Structures

Collective Coordinate Control of Density Distributions

- **Microscopic density** $\rho(\mathbf{r})$ **of a system of** N **particles in fundamental region** Ω **at position** $\mathbf{r}$ **is**

$$\rho(\mathbf{r}) = \sum_{j=1}^{N} \delta(\mathbf{r} - \mathbf{r}_j)$$

- **The corresponding complex collective density variable is defined by**

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- **The nonnegative structure factor is**

$$S(\mathbf{k}) = \frac{|\rho(\mathbf{k})|^{\mathbf{2}}}{\mathbf{N}} = \mathbf{1} + \frac{\mathbf{2}}{\mathbf{N}} \mathbf{C}(\mathbf{k})$$

where $C(\mathbf{k})$ is the real collective density variable.

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where $C(\mathbf{k})$ is the **real** collective density variable.

- Consider stable radial pair potentials $v(r)$ that are **bounded** and **absolutely integrable**:

$$\Phi_N(\mathbf{r}^N) = \sum_{i<j} v(r_{ij})$$

Disordered (Highly Irregular) Ground-State Structures

- **Alternatively, we have the Fourier representation:**

$$\Phi_N = \frac{1}{|\Omega|}\sum_{\mathbf{k}} \tilde{v}(k)C(\mathbf{k}) \qquad \left[S(\mathbf{k}) = \mathbf{1} + \frac{\mathbf{2}}{\mathbf{N}}\mathbf{C}(\mathbf{k})\right]$$

where $\tilde{v}(k)$ is the Fourier transform of $v(r)$.

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$$\Phi_N = \frac{1}{|\Omega|}\sum_{\mathbf{k}} \tilde{v}(k) C(\mathbf{k}) \qquad \left[S(\mathbf{k}) = \mathbf{1} + \frac{\mathbf{2}}{\mathbf{N}}\mathbf{C}(\mathbf{k})\right]$$

where $\tilde{v}(k)$ is the Fourier transform of $v(r)$.

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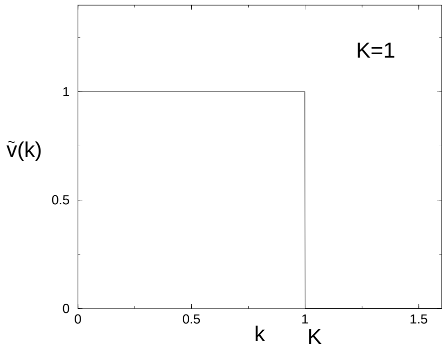

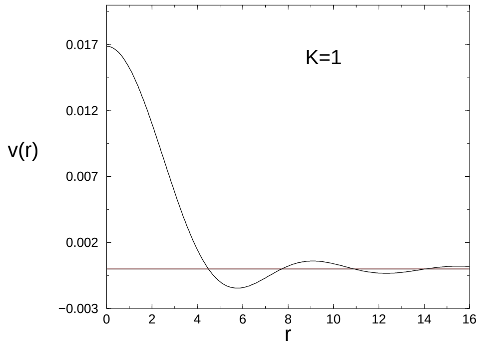

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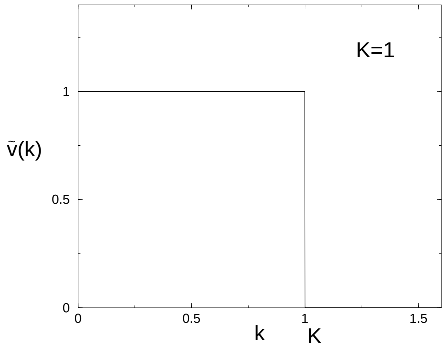
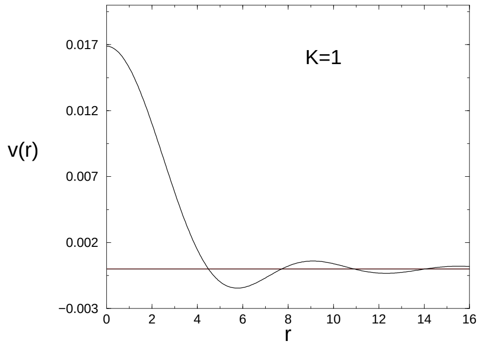
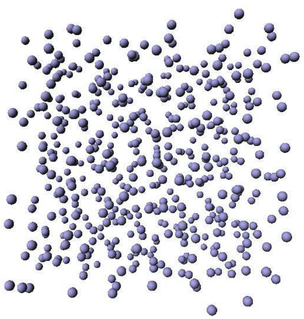


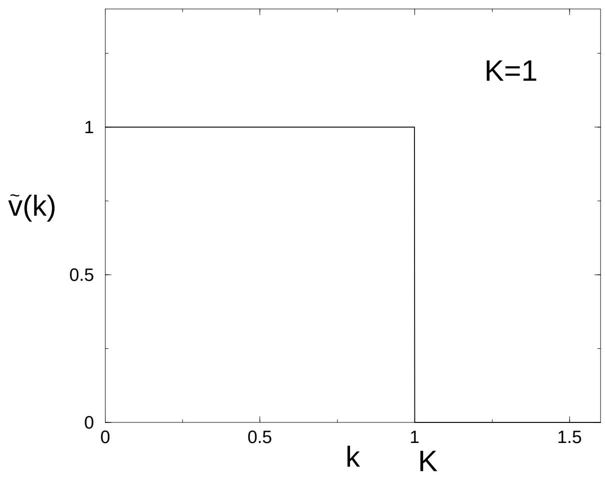


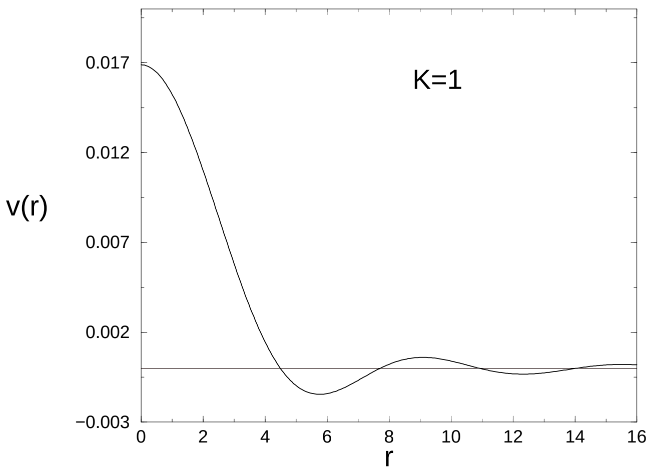
- **For sufficiently small K, the ground states are degenerate and disordered:**



Batten, Stillinger & Torquato, J. Appl. Phys., 2008

Ground States Via Collective-Coordinate Control





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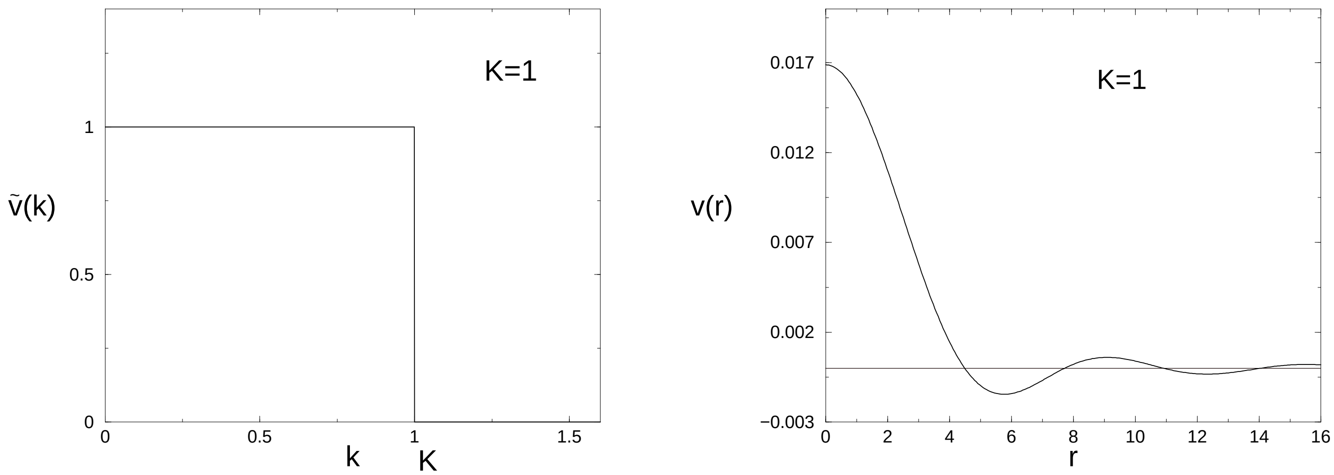

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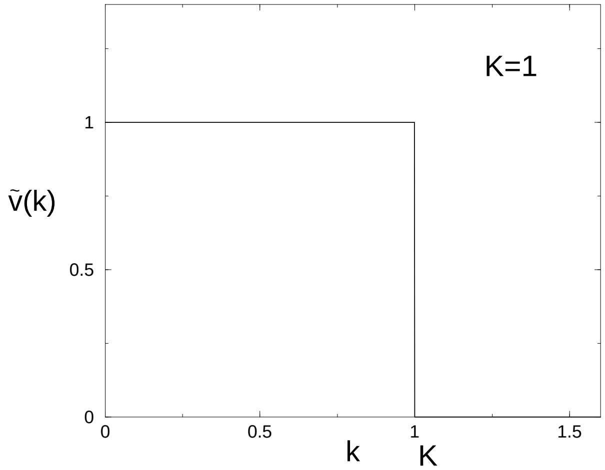

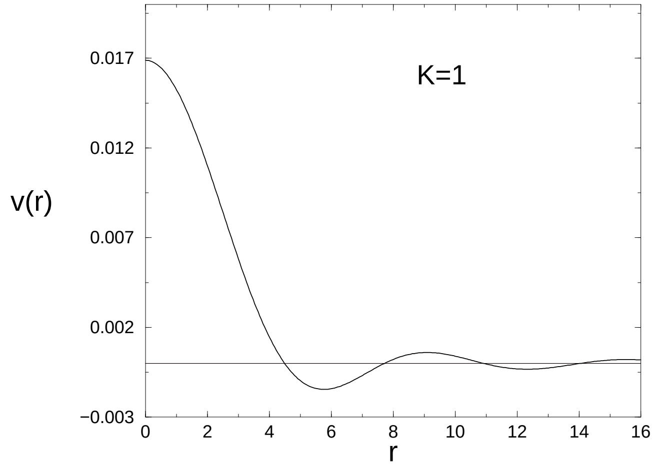

- **Sütô (PRL, 2005) showed that this class of potentials “localized” in Fourier space yield both BCC and FCC lattice ground states in $\mathbb{R}^3$ for certain densities or large enough K.**
- **Some might regard such non-localized real-space potentials as unphysical.**
- **What can we say about a localized real-space potentials?**

Duality Relation in Ensemble Setting

- **Define**

$$U(\mathbf{r}^N) = \frac{1}{N} \sum_{i=1,j=1} v(r_{ij}),$$

which is twice the total potential energy per particle plus the self-energy $v(0)$.

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- **The ensemble average of U in the thermodynamic limit is given by**

$$\langle U(\mathbf{r}^N)\rangle \quad = \quad v(r=0) + \rho \int_{\mathbb{R}^d} v(r) g_2(r) d\mathbf{r}$$

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- **Lemma: For any ergodic configuration in $\mathbb{R}^d$, the following duality relation holds:**

$$\int_{\mathbb{R}^d} v(r)h(r)d\mathbf{r} = \frac{1}{(2\pi)^d} \int_{\mathbb{R}^d} \tilde{v}(k)\tilde{h}(k)d\mathbf{k}$$

where $h(\mathbf{r}) = g_2(\mathbf{r}) - 1$ is the total correlation function.

If it is a ground state, then both sides of equation are minimized.

- **This duality relation offers an efficient means of computing total energy when either $v(r)$ or $\tilde{v}(k)$ is long-ranged.**

Duality Theorem

If an admissible pair potential $v(r)$ has a lattice ground-state structure Λ at number density ρ, we have the following duality relation for the minumum U_{min} of U:

$$v(r=0) + {\sum_{\mathbf{r}\in\Lambda}}' v(r) = \rho\tilde{v}(k=0) + \rho {\sum_{\mathbf{k}\in\tilde{\Lambda}}}' \tilde{v}(k), \qquad \textbf{(1)}$$

$\tilde{\Lambda}$ denotes the reciprocal lattice, and $\tilde{v}(k)$ is the dual pair potential, which automatically satisfies the stability condition, and therefore is admissible.

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$\tilde{\Lambda}$ denotes the reciprocal lattice, and $\tilde{v}(k)$ is the dual pair potential, which automatically satisfies the stability condition, and therefore is admissible. Moreover, the minimum $\tilde{U}_{min}$ of U for any ground-state structure of the dual potential $\tilde{v}(k)$, is bounded from above by the corresponding real-space minimized quantity U_{min} or, equivalently, the right side of (1), i.e.,

$$\tilde{U}_{min} \leq U_{min} = \rho\tilde{v}(k=0) + \rho \sum_{\mathbf{k}\in\tilde{\Lambda}}{}' \tilde{v}(k) \qquad \textbf{(2)}$$

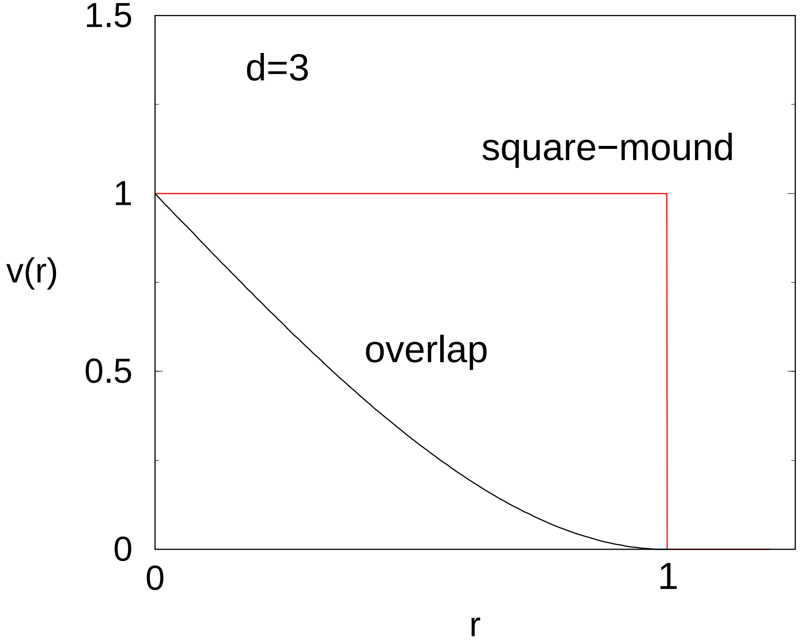
Whenever the reciprocal lattice $\tilde{\Lambda}$ at reciprocal lattice density $\tilde{\rho} = \rho^{-1}(2\pi)^{-d}$ is a ground state of $\tilde{v}(k)$, the inequality in (2) becomes an equality.

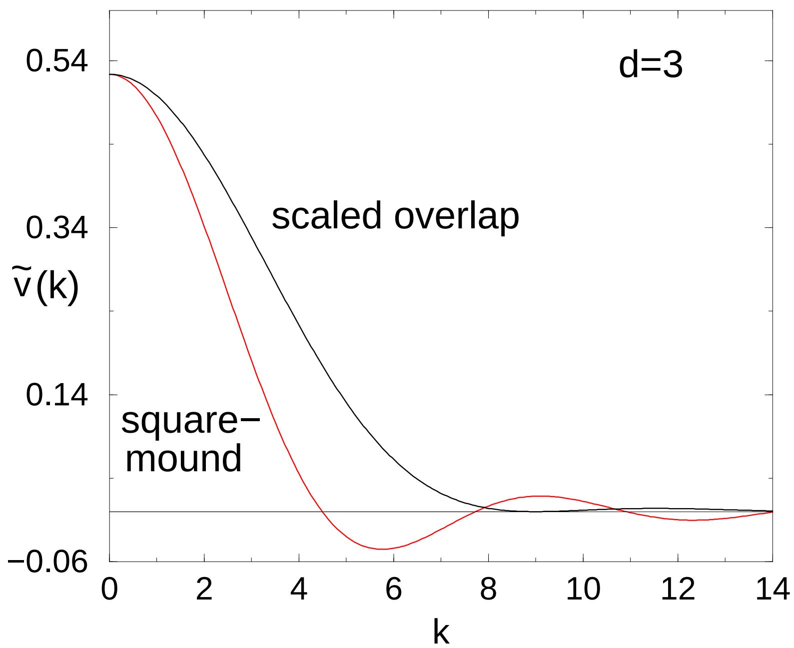
Applications and Questions

- Inequality (2) provides a computational tool to estimate ground-state energies or eliminate candidate ground-state structures in MC and MD simulations.
- Information about ground states of short-ranged potentials can be used to draw interesting conclusions about the nature of the ground states of long-ranged potentials and vice versa.
- Is the equality of relation (2) of the Theorem ever applicable? If not, can examples be constructed that establish the strict inequality?

Example 1: Localized Real-Space Potentials in $\mathbb{R}^3$

- We've shown that **localized** real-space potentials in $\mathbb{R}^3$ will have **BCC and FCC lattice ground states** at certain densities, and thus **equality** in relation (2) is established.





Example 2: One-Dimensional Ground States

- **Consider following pair potential $v(r)$ and its dual $\tilde{v}(k)$ in $\mathbb{R}$:**

$$v(r) = \left[1 - \frac{r}{2R}\right], \qquad \tilde{v}(k) = \frac{2R\sin^2(kR)}{(kR)^2}$$

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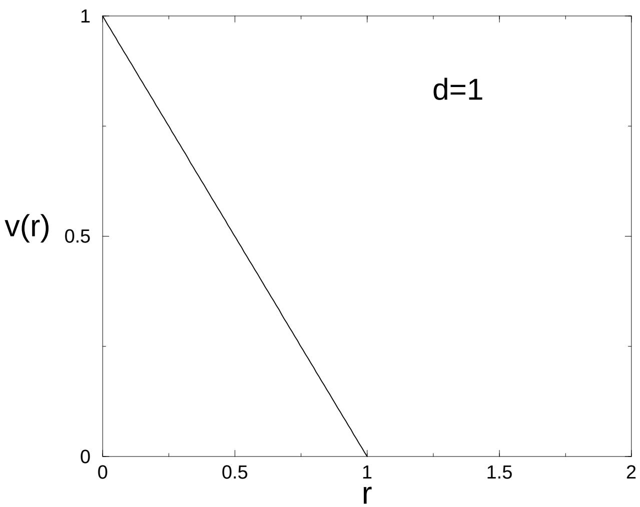

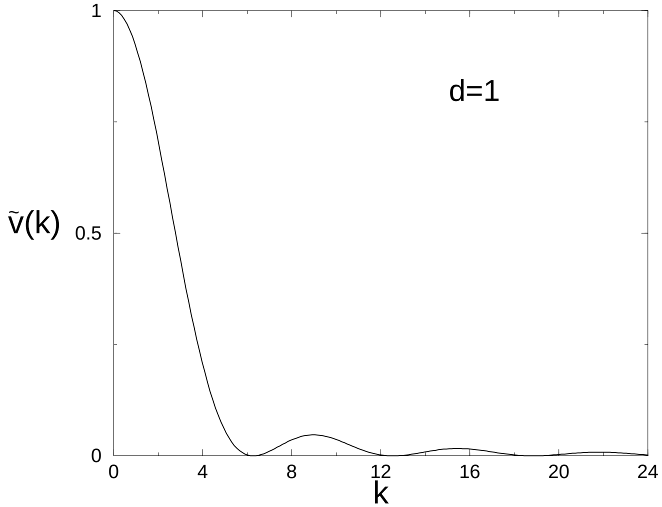

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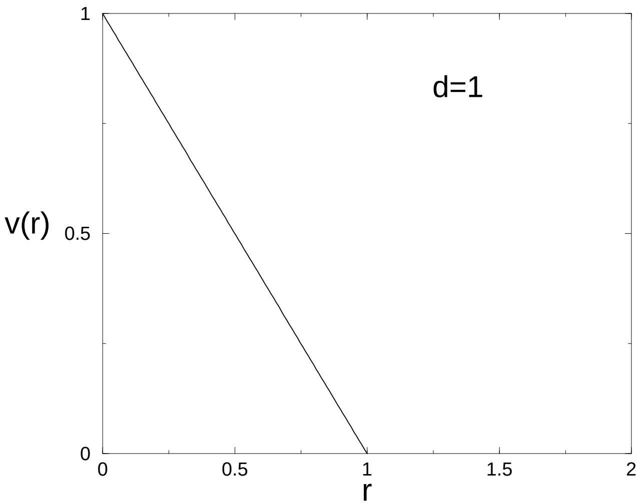

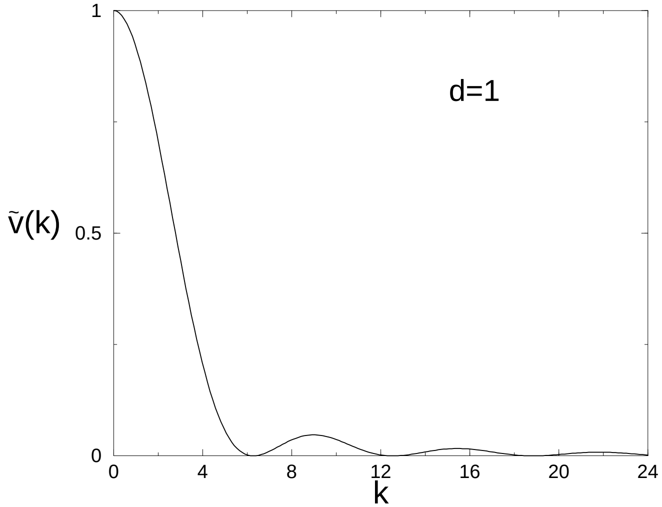

- **For any density ρ, integer lattice with spacing $1/\rho$ is the unique ground state. Moreover, for $\rho = m$ ($m = 1, 2, \ldots$), integer lattice at reciprocal density $\tilde{\rho} = (2\pi m)^{-1}$ is the ground state for $\tilde{v}(k)$.**

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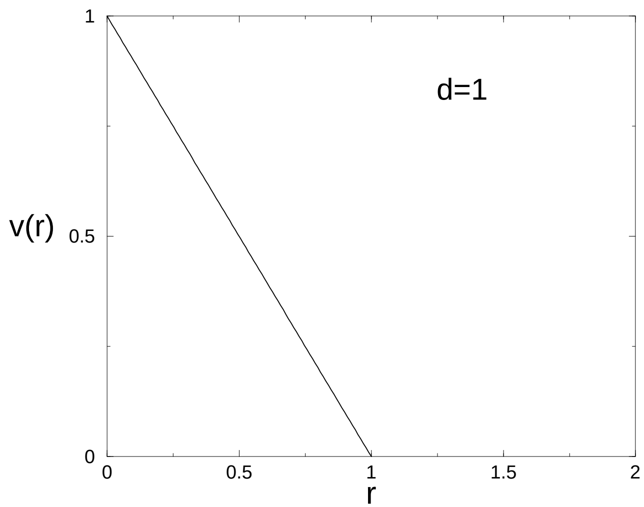

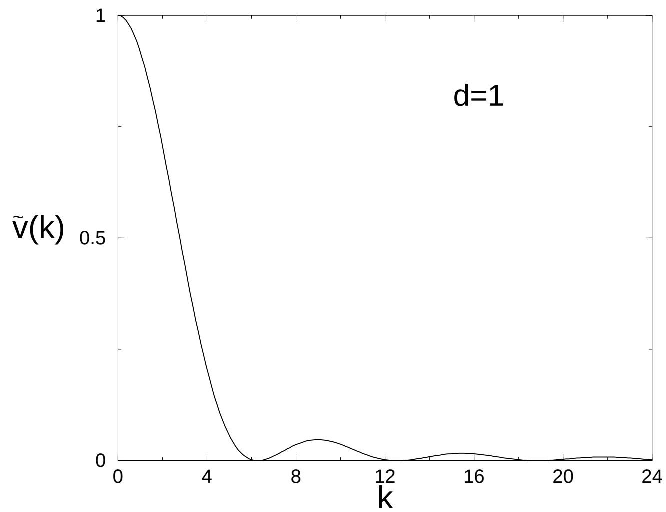

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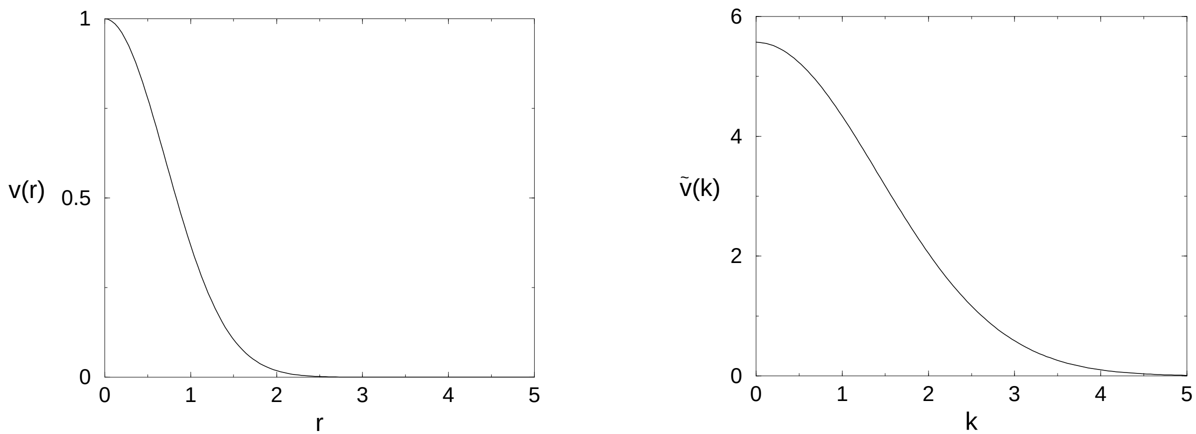
- **At noninteger density ρ, the ground state for $\tilde{v}(k)$ is generally a non-lattice, establishing the strict inequality of relation (2). This implies an infinite number of phase transitions!**

Example 3: “Gaussian-Core" Potential in $\mathbb{R}^3$

- **Useful model interaction for polymers.**
- **At low and high densities, FCC and BCC crystals are ground states, respectively, thus establishing another instance of the equality in relation (2).**

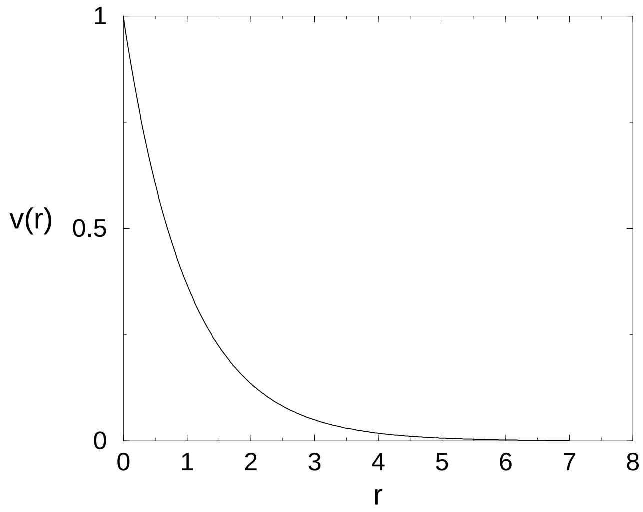


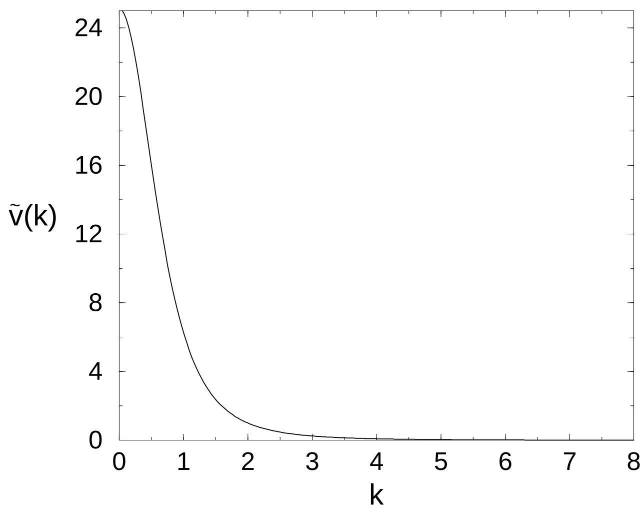
- **However, in the narrow density interval of FCC-BCC coexistence, the ground states are not lattices and can be shown to have lower energies than either FCC or BCC lattices.**
- **This work has been extended to higher dimensions (Zachary, Stillinger and Torquato 2008).**

Example 4: Completely Monotonic Potentials

- **A radial function $f(r)$ is completely monotonic if it possesses derivatives $f^{(n)}(r)$ for all $n = 0, 1, 2, \ldots$ and if $(-1)^n f^{(n)}(r) \geq 0$. An example of such as admissible potential is the following:**

$$v(r) = \exp(-r), \qquad \tilde{v}(k) = \frac{8\pi}{(1+k^2)^2}$$

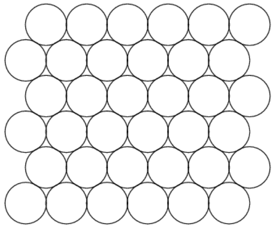




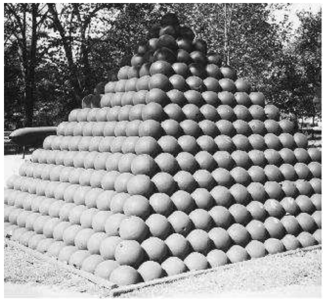
- **We believe we can show that this new class of potential functions exhibits FCC and BCC ground states using results from Cohn and Kumar, J. Am. Math. Soc. 2007.**

Sphere Packing Problem in Low Dimensions

- **For $d = 2$, solution is triangular lattice: $\phi_{\textbf{max}} = \pi/\sqrt{12} \approx 0.91$ (Fejes Tóth, 1940).**



- **For $d = 3$, Kepler (1606) conjectured that optimal packing is FCC lattice: $\phi_{\textbf{max}} = \pi/\sqrt{18} \approx 0.74$ (Hales 1998, 2005).**



- **Each dimension has its own distinct properties.**
- **In certain sufficiently low dimensions, optimal packings are believed to be lattice packings. Certain dimensions are amazingly symmetric and dense: $d = 8$ (E_8 lattice) and $d = 24$ (Leech lattice).**
- **In $\mathbb{R}^{10}$, the best known arrangement is a non-lattice packing.**

Disordered Packings Might Win in High Dimensions

- **Based on a well-founded conjecture, we derived the following lower bound on the maximal density $\phi_{\textbf{max}}$ for sphere packings in $\mathbb{R}^d$:**

$$\phi_{\textbf{max}} \geq \frac{c(d)}{2^{(0.7786...)d}},$$

which provides exponential improvement over Minkowski's 100-year-old bound ($\phi_{\textbf{max}} \geq 1/2^d$) for lattices.

Torquato and Stillinger, Exper. Math. (2006)

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- **Implies existence of disordered classical ground states for some continuous potentials in sufficiently high dimensions, i.e., stable glasses.**

- **This asymptotic form was shown to be more robust than previously thought - it might even be optimal!**

Scardicchio, Stillinger and Torquato (2008)

CONCLUSIONS

- We can tailor potentials to yield **unusual classical ground states**, including **disordered** ones as well as **low-coordinated crystals**.
- Our work suggests that the densest sphere packings are disordered in sufficiently high dimensions, implying the existence of **continuous potentials** with disordered classical ground states.

Collaborators

- **Robert Batten**, Princeton
- **Mikael Rechtsman**, Princeton/Courant
- **Antonello Scardicchio**, Princeton/ICTP, Trieste
- **Frank Stillinger**, Princeton
- **Chase Zachary**, Princeton

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