Amorphous Trivalent and Tetrahedral Networks

Salvatore Torquato

Department of Chemistry,

Department of Physics,

Princeton Institute for the Science and Technology of Materials,

and Program in Applied & Computational Mathematics

Princeton University

Growing Length Scales Under Supercooling

- A question that has received considerable attention in recent years is whether the growing relaxation times under supercooling have accompanying growing structural length scales.

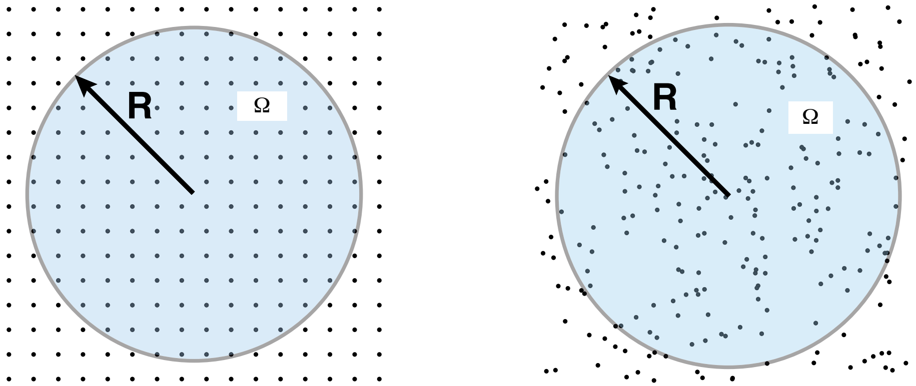
  Two distinct schools of thought have emerged to address this question:
  - One camp asserts that static structure of a glass, as measured by pair correlations, is indistinguishable from that of the corresponding liquid. There is no signature of increasing static correlation length scales accompanying the glass transition, it identifies growing dynamical length scales. Berthier, Biroli, Bouchaud, Kob, Reichman, Sastry, Chandler
  - The other camp contends that there is a static growing length scale of thermodynamic origin, and therefore one need not look for growing length scales associated with the dynamics. Lubchenko, Wolynes, Hocky, Markland, Reichman
- We have offered an alernative explanation: the existence of a growing static length scale but one that is intrinsically nonequilibrium in nature.

Marcotte, Stillinger and Torquato, J. Chem. Phys. (2013)

Local Density Fluctuations for General Point Patterns

Torquato and Stillinger, PRE (2003)

- **Points can represent molecules of a material, stars in a galaxy, or trees in a forest. Let Ω represent a spherical window of radius R in d-dimensional Euclidean space $\mathbb{R}^d$.**



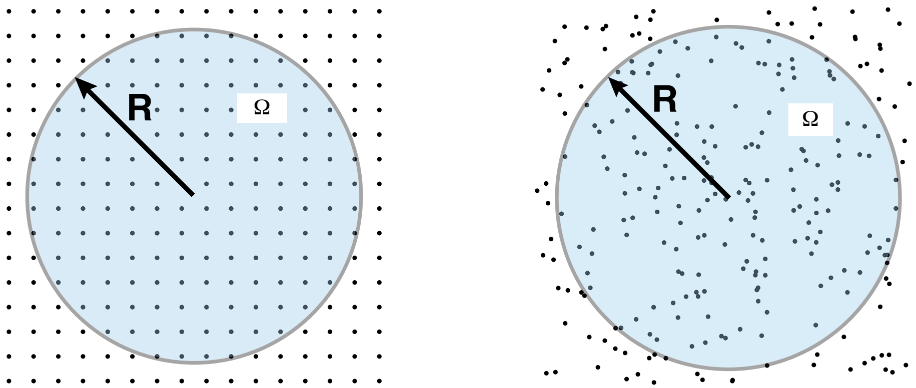
Average number of points in window of volume $v_1(R)$: $\langle N(R)\rangle = \rho v_1(R) \sim R^d$

Local number variance: $\sigma^2(R) \equiv \langle N^2(R)\rangle - \langle N(R)\rangle^2$

Local Density Fluctuations for General Point Patterns

Torquato and Stillinger, PRE (2003)

- Points can represent molecules of a material, stars in a galaxy, or trees in a forest. Let Ω represent a spherical window of radius R in d-dimensional Euclidean space $\mathbb{R}^d$.



Average number of points in window of volume $v_1(R)$: $\langle N(R)\rangle = \rho v_1(R) \sim R^d$

Local number variance: $\sigma^2(R) \equiv \langle N^2(R)\rangle - \langle N(R)\rangle^2$

- For a Poisson point pattern and many disordered point patterns, $\sigma^2(R) \sim R^d$.
- We call point patterns whose variance grows more slowly than R^d (window volume) hyperuniform . This implies that structure factor $S(k) \rightarrow 0$ for $k \rightarrow 0$.
- All perfect crystals and perfect quasicrystals are hyperuniform such that $\sigma^2(R) \sim R^{d-1}$: number variance grows like window surface area.

New Growing Length Scale Upon Supercooling

- $h(\mathbf{r})$ **can be divided into direct correlations, via function $c(\mathbf{r})$, and indirect correlations:**

$$\tilde{c}(\mathbf{k}) = \frac{\tilde{h}(\mathbf{k})}{1 + \rho\tilde{h}(\mathbf{k})}$$

New Growing Length Scale Upon Supercooling

- $h(\mathbf{r})$ can be divided into direct correlations, via function $c(\mathbf{r})$, and indirect correlations:

$$\tilde{c}(\mathbf{k}) = \frac{\tilde{h}(\mathbf{k})}{1+\rho\tilde{h}(\mathbf{k})}$$

- For any hyperuniform system, $\tilde{h}(\mathbf{k}=\mathbf{0}) = -1/\rho$, and thus $\tilde{c}(\mathbf{k}=\mathbf{0}) = -\infty$. Therefore, at the "critical" reduced density ϕ_c, $h(\mathbf{r})$ is short-ranged and $c(\mathbf{r})$ is long-ranged.

- This is the inverse of the behavior at liquid-gas (or magnetic) critical points, where $h(\mathbf{r})$ is long-ranged (compressibility or susceptibility diverges) and $c(\mathbf{r})$ is short-ranged.

New Growing Length Scale Upon Supercooling

- $h(\mathbf{r})$ can be divided into direct correlations, via function $c(\mathbf{r})$, and indirect correlations:

$$\tilde{c}(\mathbf{k}) = \frac{\tilde{h}(\mathbf{k})}{1+\rho\tilde{h}(\mathbf{k})}$$

- For any hyperuniform system, $\tilde{h}(\mathbf{k}=\mathbf{0}) = -1/\rho$, and thus $\tilde{c}(\mathbf{k}=\mathbf{0}) = -\infty$. Therefore, at the “critical” reduced density ϕ_c, $h(\mathbf{r})$ is short-ranged and $c(\mathbf{r})$ is long-ranged.

- This is the inverse of the behavior at liquid-gas (or magnetic) critical points, where $h(\mathbf{r})$ is long-ranged (compressibility or susceptibility diverges) and $c(\mathbf{r})$ is short-ranged.

- For sufficiently large d at a disordered hyperuniform state, whether achieved via a nonequilibrium or an equilibrium route,

$$\begin{array}{llll} c(\mathbf{r}) \sim -\dfrac{1}{r^{d-2+\eta}} & (r \rightarrow \infty), & \tilde{c}(\mathbf{k}) \sim -\dfrac{1}{k^{2-\eta}} & (k \rightarrow 0), \\ h(\mathbf{r}) \sim -\dfrac{1}{r^{d+2-\eta}} & (r \rightarrow \infty), & S(\mathbf{k}) \sim k^{2-\eta} & (k \rightarrow 0), \end{array}$$

  where η is a new critical exponent and d is the Euclidean space dimension. .

- From the Fourier transform of the direct correlation function $c(k)$, which has units of volume, we define the following length scale:

$$\xi_c \equiv [-\tilde{c}(k=0)]^{1/d} = \left[-\int_{\mathbb{R}^d} c(r)d\mathbf{r}\right]^{1/d}$$

Remarks About Equilibrium Systems

- **For single-component systems in equilibrium at average number density ρ,**

$$\rho k_B T \kappa_T = \frac{\langle N^2 \rangle_* - \langle N \rangle_*^2}{\langle N \rangle_*} = S(\mathbf{k}=\mathbf{0}) = 1 + \rho \int_{\mathbb{R}^d} h(\mathbf{r}) d\mathbf{r}$$

where $\langle \rangle_*$ denotes an average in the grand canonical ensemble.

Some observations:

  - **Any ground state ($T = 0$) in which the isothermal compressibility κ_T is bounded and positive must be hyperuniform. This includes crystal ground states as well as exotic disordered ground states, described later.**
  - **However, in order to have a hyperuniform system at positive T, the isothermal compressibility must be zero; i.e., the system must be incompressible.**

- **Note that generally $\rho k T \kappa_T \neq S(\mathbf{k}=\mathbf{0})$.**

$$X = \frac{S(\mathbf{k}=\mathbf{0})}{\rho k_B T \kappa_T} - 1 : \quad \text{Nonequilibrium index}$$

Structural Glasses and Growing Length Scales

- **Important question in glass physics: Do growing relaxation times under supercooling have accompanying growing structural length scales?** **Lubchenko & Wolynes (2006); Berthier et al. (2007); Karmakar, Dasgupta & Sastry (2009); Chandler & Garrahan (2010); Hocky, Markland & Reichman (2012)**

Structural Glasses and Growing Length Scales

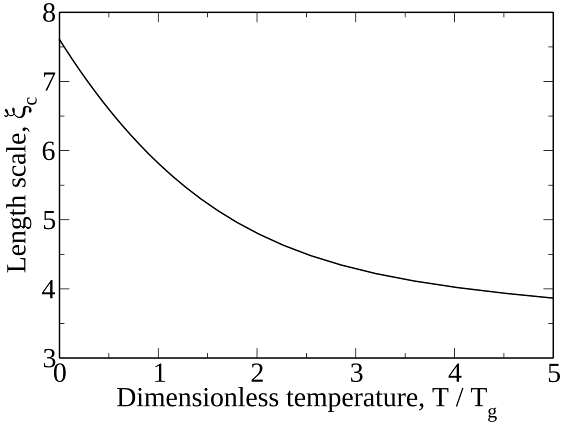
- **Important question in glass physics: Do growing relaxation times under supercooling have accompanying growing structural length scales? Lubchenko & Wolynes (2006); Berthier et al. (2007); Karmakar, Dasgupta & Sastry (2009); Chandler & Garrahan (2010); Hocky, Markland & Reichman (2012)**
- **We studied glass-forming liquid models that support an alternative view: existence of growing static length scales (due to increase of the degree of hyperuniformity) as the temperature T of the supercooled liquid is decreased to and below T_g that is intrinsically nonequilibrium in nature.**
- **The degree of deviation from thermal equilibrium is determined from a nonequilibrium index**

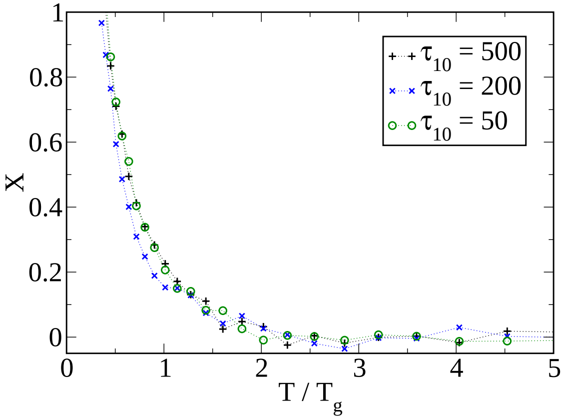
$$X = \frac{S(\mathbf{k}=\mathbf{0})}{\rho k_B T \kappa_T} - 1.$$

Structural Glasses and Growing Length Scales

- **Important question in glass physics: Do growing relaxation times under supercooling have accompanying growing structural length scales? Lubchenko & Wolynes (2006); Berthier et al. (2007); Karmakar, Dasgupta & Sastry (2009); Chandler & Garrahan (2010); Hocky, Markland & Reichman (2012)**
- **We studied glass-forming liquid models that support an alternative view: existence of growing static length scales (due to increase of the degree of hyperuniformity) as the temperature T of the supercooled liquid is decreased to and below T_g that is intrinsically nonequilibrium in nature.**
- **The degree of deviation from thermal equilibrium is determined from a nonequilibrium index**

$$X = \frac{S(\mathbf{k} = \mathbf{0})}{\rho k_B T \kappa_T} - 1.$$

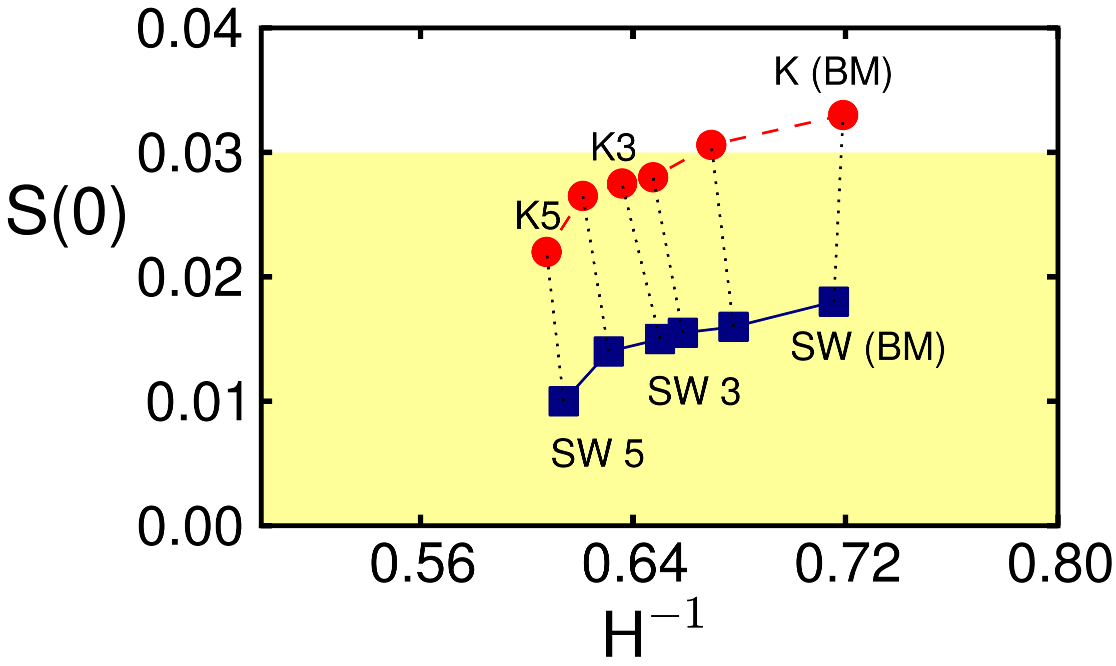




Nearly Hyperuniform Network Models of Amorphous Silicon

- Conventional continuous random network (CRN) models for a-Si are fully four-coordinated, isotropic disordered networks that contain primarily five, six, and seven atom rings, while maintaining nearly perfect local tetrahedral order (narrow bond-angle and bond-length distributions).
- Predictions derived from CRN models using a Keating potential are in good agreement with many structural properties of a-Si that are accessible via experiments, including g_2, phonon and electron density of states, nearest- and next-nearest-neighbor distances, bond statistics, ring statistics, etc. These successes are related to the form of $S(k)$ at intermediate wavenumbers.
- Previous Keating-model studies have yielded $S(0) \approx 0.03$.
- We define a nearly hyperuniform network (NHN) to be a disordered tetrahedral structure whose $S(0)$ is less than the liquid value at melting.
- Particulary interested in cases where $S(0)$ is reduced by at least 50/in the large-scale density fluctuations and runs counter to the limitations imposed by the frozen-liquid paradigm.
- We used a two-step numerical protocol to produce a spectrum of NHN models:
  1. Step one is a standard bond-switching annealing procedure using a Keating potential applied to 20,000 atoms under PBCs. Unlike Barkema-Mousseau (PRB 2000), we anneal our systems significantly longer to achieve a sequence of inherent structures (local potential-energy minima) that have lower energies than those of the BM model.
  2. In the second, we use our end-state inherent-structure configurations obtained via a Keating potential (K1, K2, etc.) as initial conditions for atomic-position rearrangement under a Stillinger-Weber (SW) potential at zero pressure via a conjugate gradient method.

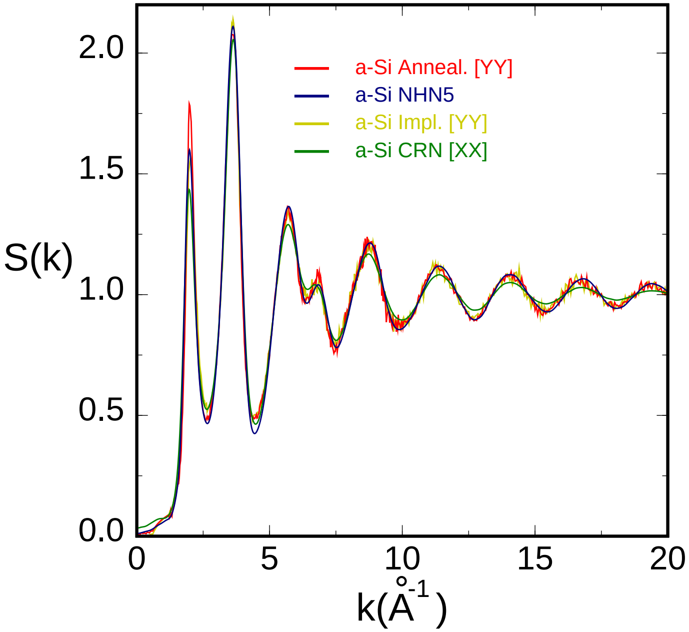
Nearly Hyperuniform Network Models of Amorphous Silicon



- **Increasing the degree of hyperuniformity of a-Si appears to be correlated with a larger electronic band gap (Hejna, Steinhardt and Torquato, 2013).**

Amorphous Silicon is Nearly Hyperuniform

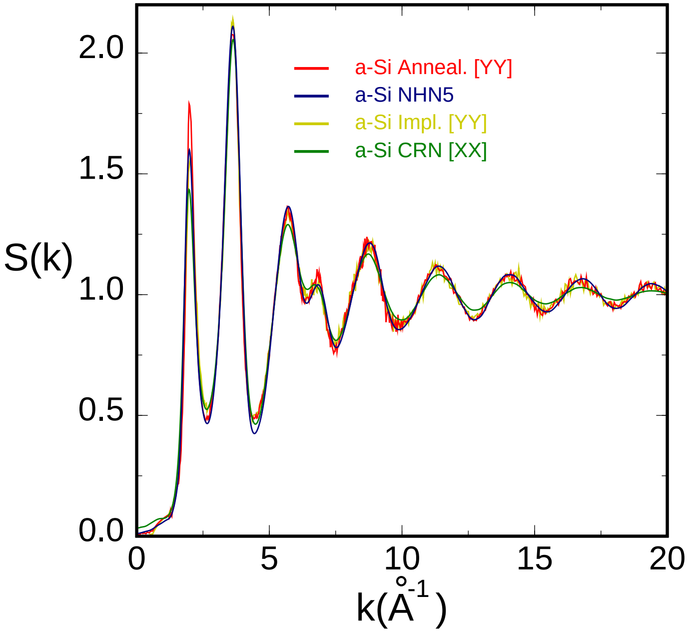
- **Highly sensitive transmission X-ray scattering measurements performed at Argonne on amorphous-silicon (a-Si) samples reveals that they are nearly hyperuniform with $S(0) = 0.0075$.**



Long, Roorda, Hejna, Torquato, and Steinhardt (2013)

Amorphous Silicon is Nearly Hyperuniform

- **Highly sensitive transmission X-ray scattering measurements performed at Argonne on amorphous-silicon (a-Si) samples reveals that they are nearly hyperuniform with $S(0) = 0.0075$.**



Long, Roorda, Hejna, Torquato, and Steinhardt (2013)

- **This is significantly below the putative lower bound recently suggested by de Graff and Thorpe (2009) but consistent with the recently proposed nearly hyperuniform network picture of a-Si (Hejna, Steinhardt and Torquato, 2013).**

Inverse Statistical Mechanics

Torquato, Soft Matter (2009)

- Two-fold objective:
  1. Statistical-mechanical methodology to find interaction potential in many-body systems that lead spontaneously to a "target" structure.
  2. Then apply this knowledge to create de novo colloidal and/or polymer systems with tuned interactions that result in these structures.

Inverse Statistical Mechanics

Torquato, Soft Matter (2009)

- **Two-fold objective:**
  1. **Statistical-mechanical methodology to find interaction potential in many-body systems that lead spontaneously to a "target" structure.**
  2. **Then apply this knowledge to create de novo colloidal and/or polymer systems with tuned interactions that result in these structures.**
- **Why colloids? Both repulsive and attractive interactions can be tuned:**
  - **exclusion volume (repulsive)**
  - **electrostatic (repulsive/attractive)**
  - **surface modification with polymers (repulsive)**
  - **depletion (attractive)**
  - **alternating fields (repulsive/attractive)**

  Therefore, offer a myriad of possible potentials that far extends the range available with molecular systems.
- **"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.**
- **Equilibrium and nonequilibrium routes can be used.**

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 radial (isotropic) 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 structure (photonic materials)
  3. effective water interactions
  4. quasicrystals
  5. amorphous structures
  6. hyperuniform systems

Designer Potentials for Targeted Configurations Via Optimization

- **General Goal**: Find interaction potential for a **target colloidal ground-state structure via optimization techniques**.

Designer Potentials for Targeted Configurations Via Optimization

- **General Goal: Find interaction potential for a target colloidal ground-state structure via optimization techniques.**

- **Specific Goal: Determine limitations of isotropic pair potentials. For example, are there low-coordinated crystal ground states?**

Designer Potentials for Targeted Configurations Via Optimization

- **General Goal**: Find interaction potential for a **target colloidal ground-state structure via optimization techniques**.

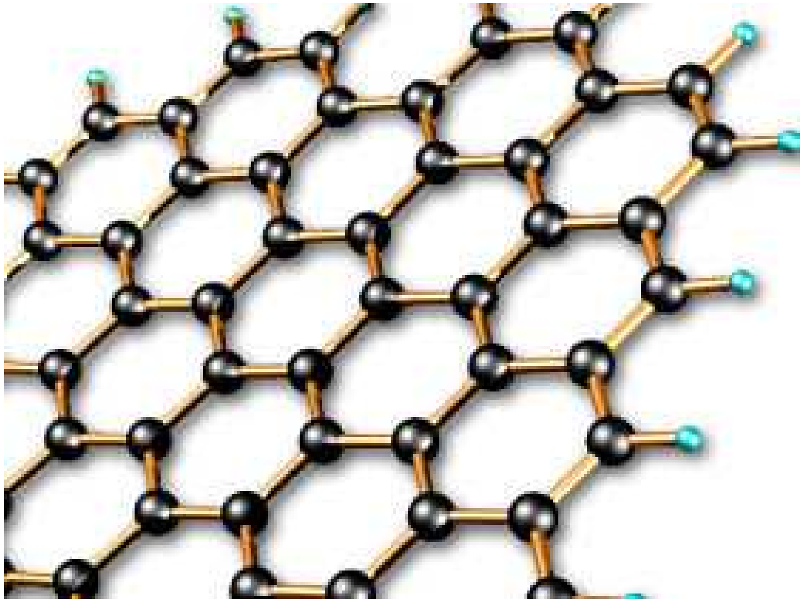
- **Specific Goal:** Determine limitations of **isotropic** pair potentials. For example, are there **low-coordinated crystal** ground states?

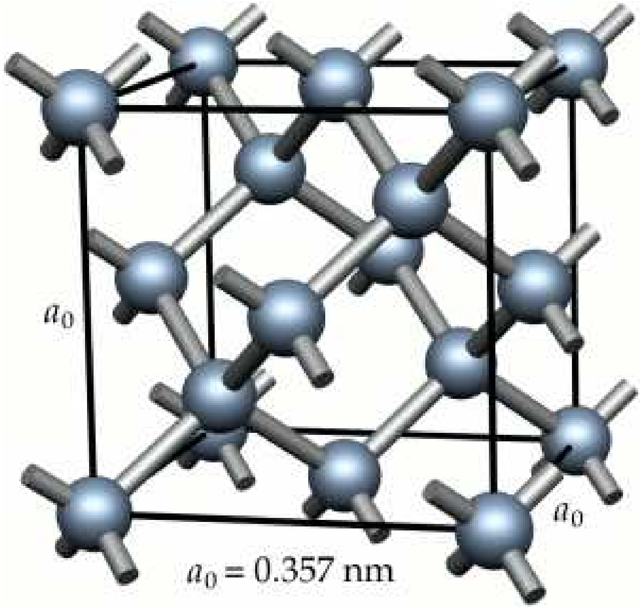
- Standard short-range interactions often lead to **close-packed crystals as ground states**.

Designer Potentials for Targeted Configurations Via Optimization

- **General Goal**: Find interaction potential for a **target colloidal ground-state structure via optimization techniques**.
- **Specific Goal:** Determine limitations of **isotropic** pair potentials. For example, are there **low-coordinated crystal** ground states?
- Standard short-range interactions often lead to **close-packed crystals as ground states**.

Graphene or Diamond Crystal With Non-Directional Interactions?



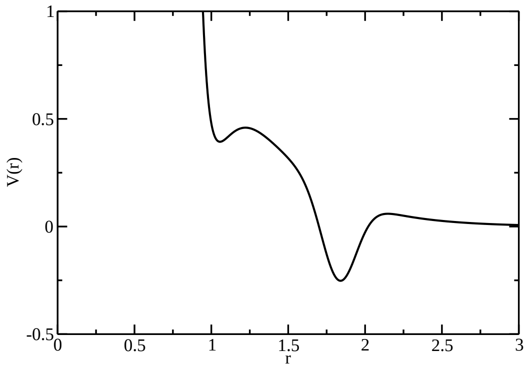


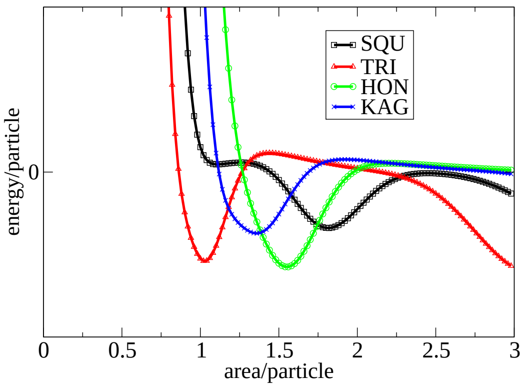
Graphene as Ground State of an Isotropic Interaction

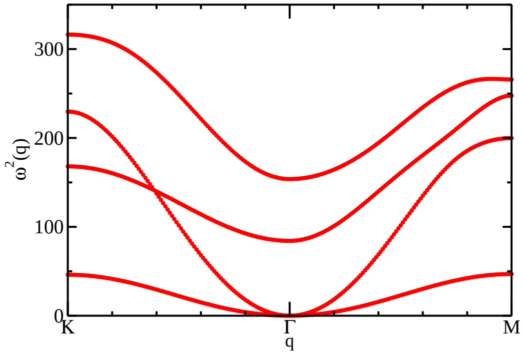
- **Optimization criteria:** favorable lattice sums and phonon spectra over the **widest possible density range**, defects cost energy, etc.

Graphene as Ground State of an Isotropic Interaction

- **Optimization criteria:** favorable lattice sums and phonon spectra over the **widest possible density range**, defects cost energy, etc.

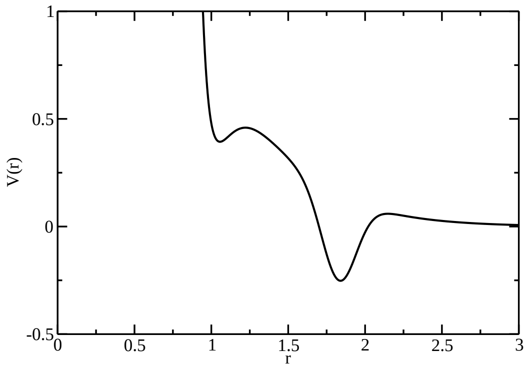


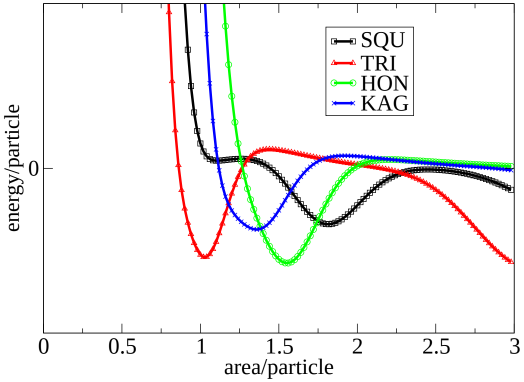


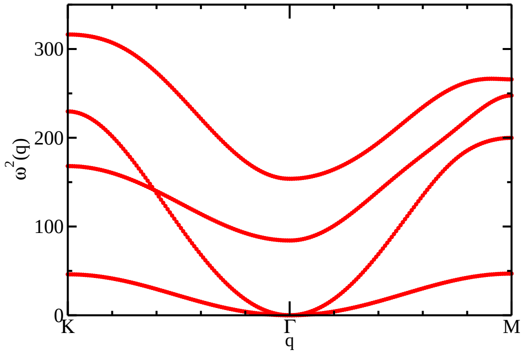


Graphene as Ground State of an Isotropic Interaction

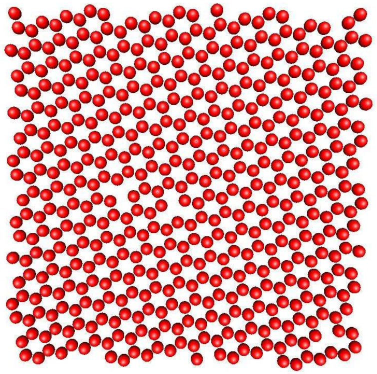
- **Optimization criteria:** favorable lattice sums and phonon spectra over the **widest possible density range**, defects cost energy, etc.







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



Rechtsman, Stillinger & Torquato, Physical Review Letters, 2005

What Are Limitations of Isotropic Interactions?

- Can one produce solid forms of carbon? Diamond? Graphite? Buckyballs?

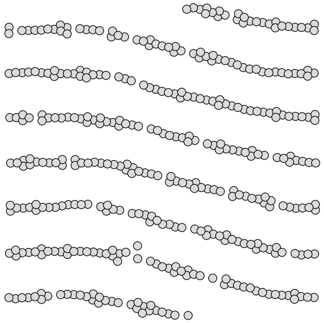
  Diamond - Yes! Rechtsman, Stillinger & Torquato, Phys. Rev. E, 2007

What Are Limitations of Isotropic Interactions?

- **Can one produce solid forms of carbon? Diamond? Graphite? Buckyballs?**

  Diamond - Yes!   Rechtsman, Stillinger & Torquato, Phys. Rev. E, 2007

- **Can one produce linear polymers?**



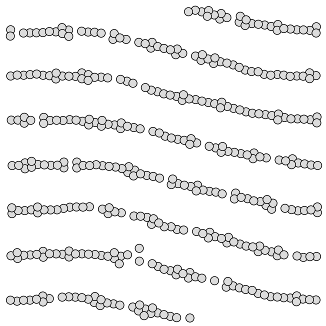
Rechtsman, Stillinger & Torquato, Phys. Rev. E, 2005

What Are Limitations of Isotropic Interactions?

- **Can one produce solid forms of carbon? Diamond? Graphite? Buckyballs?**

Diamond - Yes!   Rechtsman, Stillinger & Torquato, Phys. Rev. E, 2007

- **Can one produce linear polymers?**



Rechtsman, Stillinger & Torquato, Phys. Rev. E, 2005

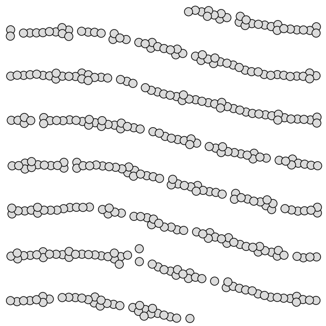
- **Can one produce single-component materials with negative thermal expansion or negative Poisson's ratio? Yes!   Rechtsman et al., JPC, 2007; PRL, 2008**

What Are Limitations of Isotropic Interactions?

- **Can one produce solid forms of carbon? Diamond? Graphite? Buckyballs?**

Diamond - Yes! Rechtsman, Stillinger & Torquato, Phys. Rev. E, 2007

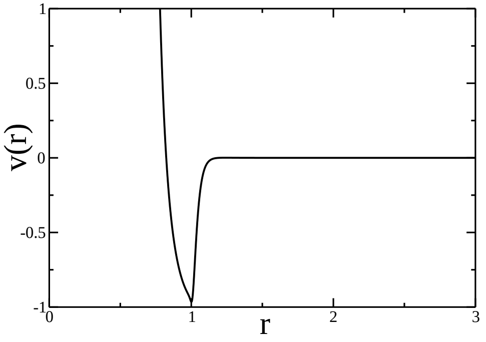
- **Can one produce linear polymers?**



Rechtsman, Stillinger & Torquato, Phys. Rev. E, 2005

- **Can one produce single-component materials with negative thermal expansion or negative Poisson's ratio? Yes! Rechtsman et al., JPC, 2007; PRL, 2008**

Can be accomplished with single minimum. For example,



What Are Limitations of Isotropic Interactions?

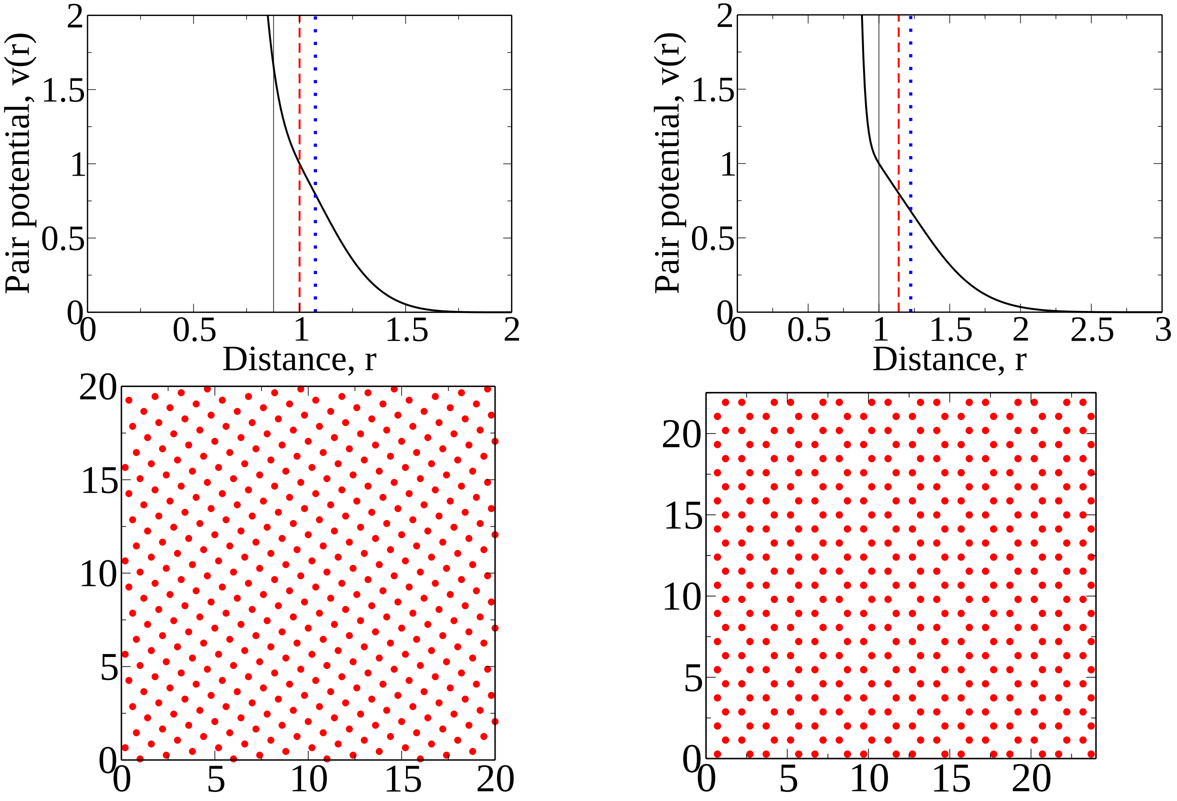
- **Can repulsive monotonic potentials stabilize low-coordinated crystals? Yes!**

  Marcotte, Stillinger & Torquato, J. Chem. Phys. (2011)

What Are Limitations of Isotropic Interactions?

- **Can repulsive monotonic potentials stabilize low-coordinated crystals? Yes!**

Marcotte, Stillinger & Torquato, J. Chem. Phys. (2011)

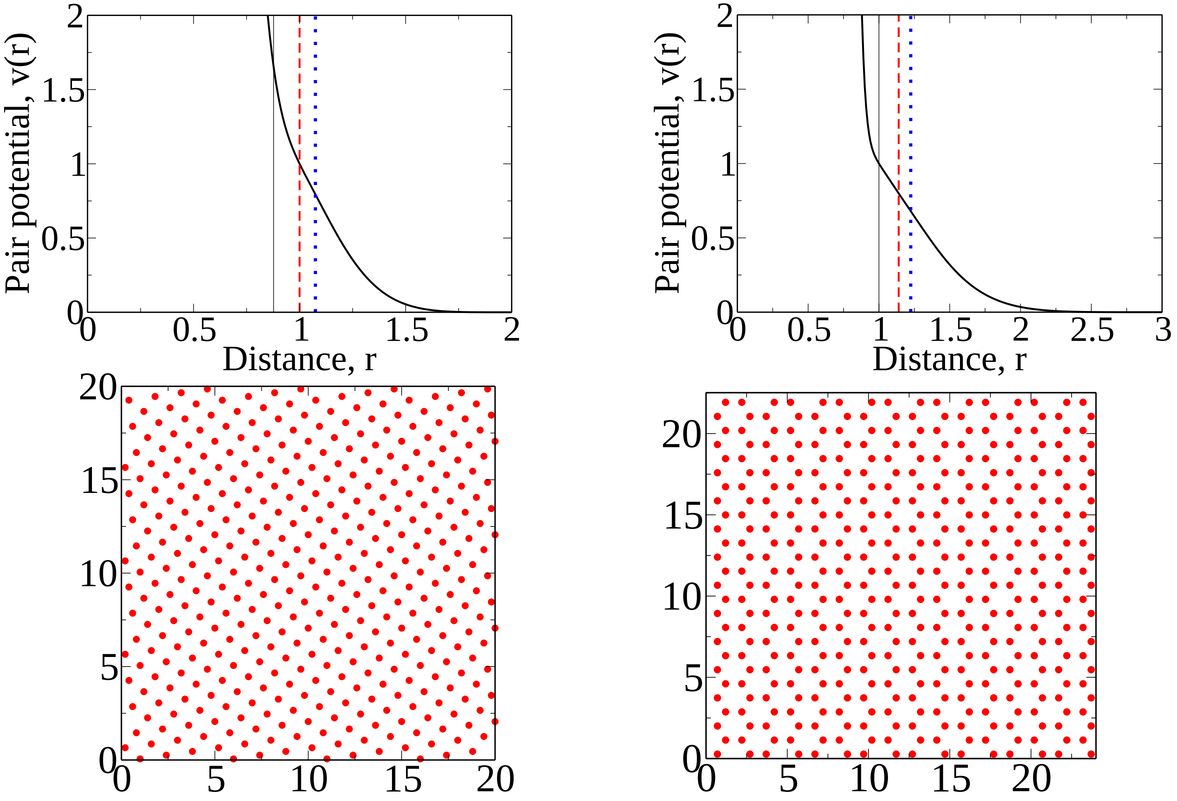


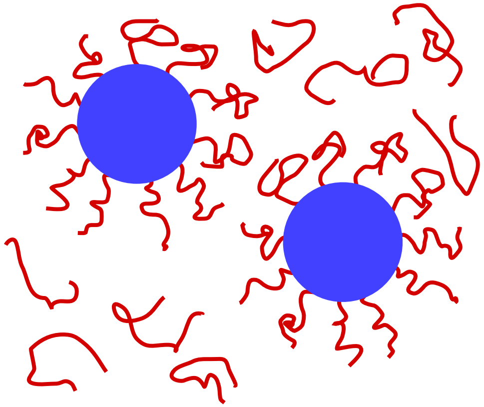
- **Systems must be under positive pressure.**

What Are Limitations of Isotropic Interactions?

- **Can repulsive monotonic potentials stabilize low-coordinated crystals? Yes!**

Marcotte, Stillinger & Torquato, J. Chem. Phys. (2011)





“Hairy Colloids”

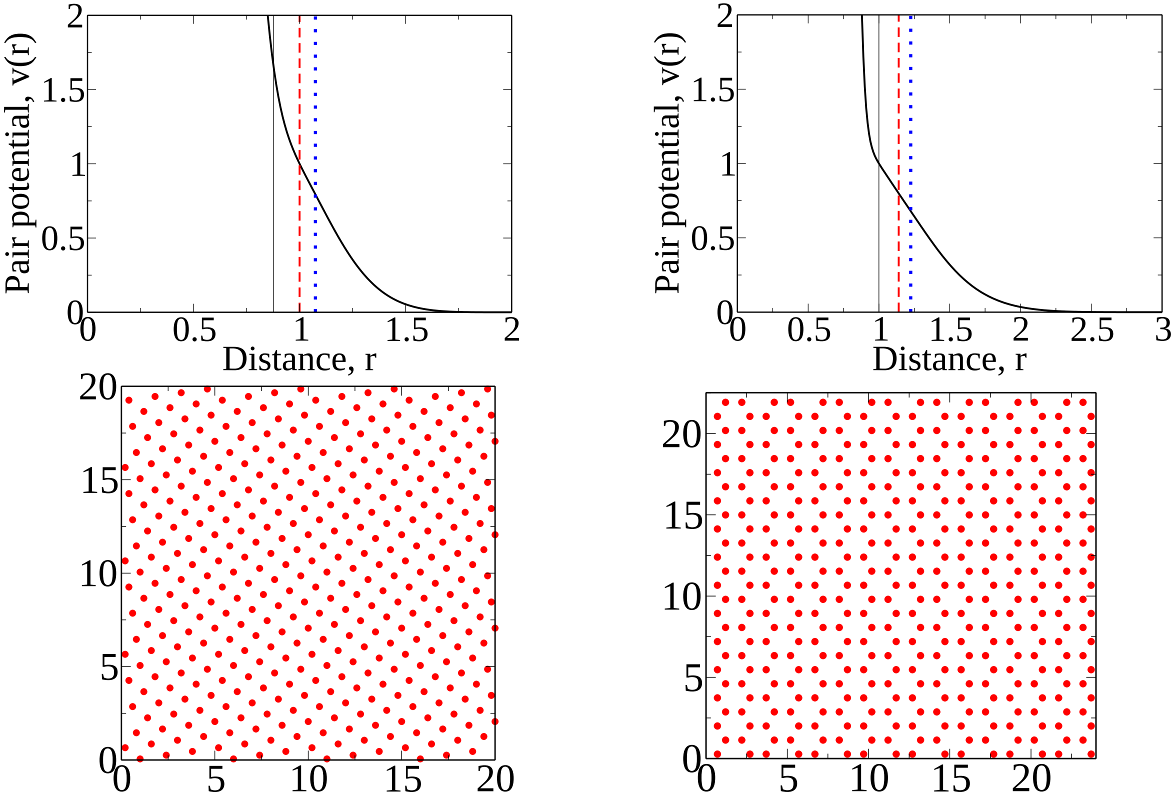
Lindenblatt et al., Macromol. (2001)

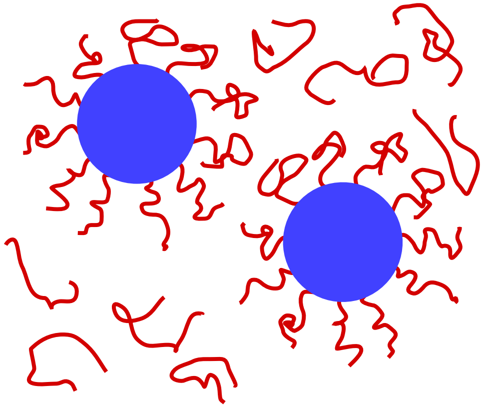
- **Systems must be under positive pressure.**

What Are Limitations of Isotropic Interactions?

- **Can repulsive monotonic potentials stabilize low-coordinated crystals? Yes!**

Marcotte, Stillinger & Torquato, J. Chem. Phys. (2011)





“Hairy Colloids”

Lindenblatt et al., Macromol. (2001)

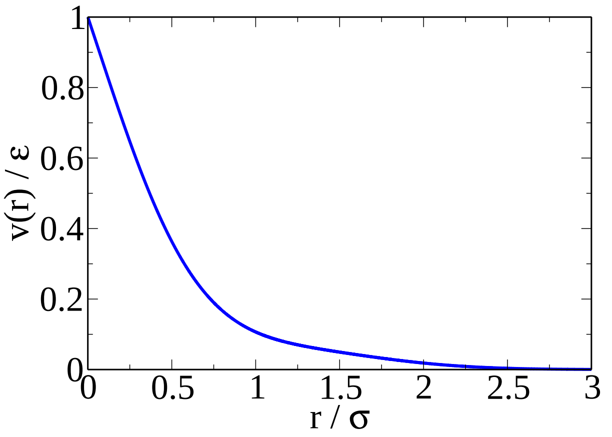
- **Systems must be under positive pressure.**

- **Can one produce vacancy-riddled ground states? Yes!**

Found a short-ranged potential whose phase diagram includes kagomé & honeycomb crystals and “striped” phases.

Batten, Huse, Stillinger & Torquato, Soft Matter (2011)

Monotonic Isotropic Potential for Diamond Crystal



$$v(r) = \varepsilon \left(1 + a_1 \frac{r}{\sigma} + a_2 \left(\frac{r}{\sigma}\right)^2\right) e^{-(r/\sigma)^2}$$

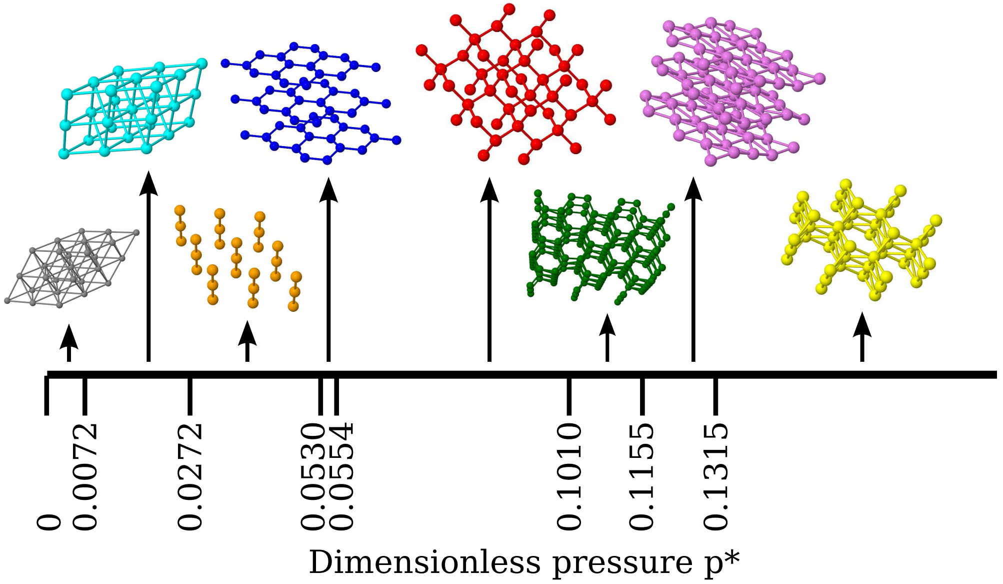


Figure 1: **Crystal phases indicated from zero pressure to higher pressures are the 12-coordinated FCC (gray), the 8-coordinated BCC (cyan), a 2-coordinated hexagonal (orange), a 3-coordinated buckled rhombohedral graphite (blue), the 4-coordinated diamond (red), a 5/6-coordinated deformed diamond (green), a 6-coordinated buckled hexagonal (violet), and a 8-coordinated flattened-hexagonal closed-**

Water-Like Anomalies from MST Potential

Bertolazzo, Kumar, Chakravarty & Molinero, J. Phys. Chem B (2016)

- **Simple isotropic two-length scale models have been extensively used to understand the origin of anomalies in complex liquids.**
- **However, single-component isotropic liquids characterized to date generally do not stabilize tetrahedral crystals, and in the few cases that they do, it was found that the liquids do not display anomalies in the region of the tetrahedral crystal.**

Water-Like Anomalies from MST Potential

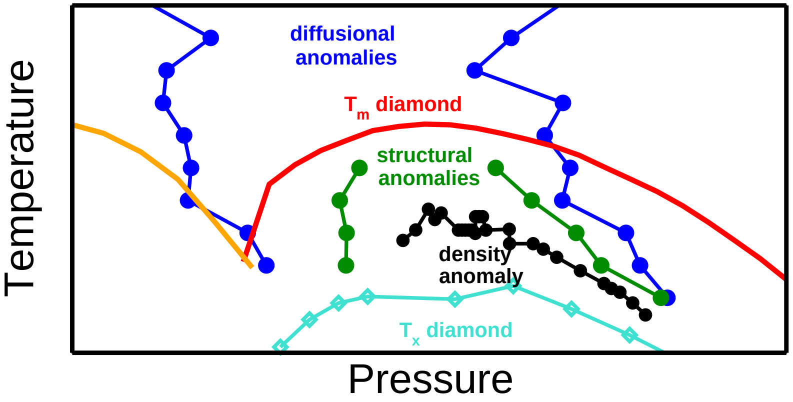
Bertolazzo, Kumar, Chakravarty & Molinero, J. Phys. Chem B (2016)

- Simple isotropic two-length scale models have been extensively used to understand the origin of anomalies in complex liquids.
- However, single-component isotropic liquids characterized to date generally do not stabilize tetrahedral crystals, and in the few cases that they do, it was found that the liquids do not display anomalies in the region of the tetrahedral crystal.
- This poses the question of whether it is possible for isotropic pair potentials to display water-like phase behavior and anomalies?

Water-Like Anomalies from MST Potential

Bertolazzo, Kumar, Chakravarty & Molinero, J. Phys. Chem B (2016)

- Simple isotropic two-length scale models have been extensively used to understand the origin of anomalies in complex liquids.
- However, single-component isotropic liquids characterized to date generally do not stabilize tetrahedral crystals, and in the few cases that they do, it was found that the liquids do not display anomalies in the region of the tetrahedral crystal.
- This poses the question of whether it is possible for isotropic pair potentials to display water-like phase behavior and anomalies?
- “We demonstrate that, akin to water, silica, and silicon, the isotropic potential of Marcotte, Stillinger, and Torquato (MST) presents structural, dynamic, and thermodynamic anomalies in the region of stability of the tetrahedral crystal. The regions of anomalies of MST are nested in the $T-p$ plane following the same hierarchy as in silica: the region of diffusional anomalies encloses the region of structural anomalies, which in turn contains the region of thermodynamic anomalies. To our knowledge, MST is the first example of pair potential for which water-like anomalies are associated with the formation of tetrahedral order.”



Keating and Stillinger-Weber Potentials

$$E_{\text{Keat.}} = \frac{3}{16}\frac{\alpha}{d^2}\sum_{i,j}\left(\mathbf{r}_{ij}\cdot\mathbf{r}_{ij} - d^2\right)^2 + \frac{3}{16}\frac{\beta}{d^2}\sum_{i,j,k}\left(\mathbf{r}_{ij}\cdot\mathbf{r}_{ik} + \frac{1}{3}d^2\right)^2 .$$

$$E_{SW} = \sum_{i,j} v_2(r_{ij}) + \sum_{i,j,k} v_3(r_{ij}, r_{ik}, \cos\theta_{ijk}),$$

$$\begin{aligned} v_2(r_{ij}) &= \varepsilon f_2\left(r_{ij}/\sigma\right), \\ v_3(r_{ij}, r_{ik}, \cos\theta_{ijk}) &= \varepsilon f_3\left(r_{ij}/\sigma, r_{ik}/\sigma, \cos\theta_{ijk}\right), \end{aligned}$$

$$f_2(r) = \begin{cases} A(Br^{-p} - r^{-q})\exp\left[(r-a)^{-1}\right] & r < a \\ 0 & r \geq a, \end{cases}$$

$$f_3(r_{ij}, r_{ik}, \cos\theta_{ijk}) = \lambda\exp\left[\gamma(r_{ij}-a)^{-1} + \gamma(r_{ik}-a)^{-1}\right]\left(\cos\theta_{ijk} + \frac{1}{3}\right)^2$$