Inventing Particle Interactions for Targeted Self-Assembly

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The recent emphasis on self assembly processes at the sub-microscopic length scale has been driven both by scientific curiosity and by the promise of significant technological applications. This situation has brought attention to a family of open problems in many-body physics. In particular it highlights the need for methods and results that deserve to be identified as "inverse statistical mechanics." This approach starts by identifying a desirable target structure, then proceeds to construct an interaction potential between particles which causes that structure to self-assemble. Such a construction can serve as a guide for experimental realization (*e.g.* in colloids).

This lecture surveys the basic concepts and strategies required, and provides a variety of examples of constructed isotropic pair potentials and their corresponding self-assembled structures. These examples include the square and honeycomb crystals in two dimensions, and the simple cubic and diamond crystals in three dimensions. The discussion also covers basic limitations of the inverse statistical mechanical approach.

SLIDES

1. Intro	11. squ-pot	21. sc-pot	31. 5finger-pot
2. Inverse	12. squ-lat	22. sc-lat	32. 5finger-mc
3. Colloid	13. squ-pho	23. sc-pho	33. simplex-pot
4. Possible	14. squ-mc	24. sc-md	34. simplex-mc
5. Tetrahedron	15. Honey	25. shex-pot	35. Final
6. Lattsums	16. hon-pot	26. DvsW	
7. Necessary	17. hon-lat	27. dia-pot	
8. LJ	18. hon-pho	28. dia-lat	
9. Optimization	19. hon-mc	29. dia-pho	
10. Square	20. PTphasediag	30. dia-md	

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INVENTING PARTICLE INTERACTIONS FOR TARGETED SELF-ASSEMBLY

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Motivations:

Helping to fill a gap in the subject of statistical mechanics
Providing insights for production of new materials and devices

Outline:

"Direct" *vs.* "inverse" methods in statistical mechanics
Controllable interactions in colloid science
Possible *vs.* impossible target structures using isotropic pair potentials (v_2)
Selection and optimization procedures for v_2's
Two-dimensional crystals:
- square
- honeycomb

Three-dimensional crystals:
- simple cubic
- simple hexagonal
- diamond

Some unusual self-assembling structures
Some challenging unsolved problems

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"DIRECT" METHODS

Start with the Hamiltonian for a many-body system of interest. Employ available techniques to deduce thermal equilibrium properties (ground state, phase diagram, ...), metastable states, and kinetic properties (viscosity, thermal conductivity, ...).

"INVERSE" METHODS

Start with a target ground-state structure. Identify the family of isotropic pair potentials $v_2(r)$ producing that ground state. Optimize within that family for maximum stability and ease of assembly.

CONTROLLABLE INTERACTIONS IN COLLOID SCIENCE

Effective pair interactions (potentials of mean force) in colloidal suspensions can be manipulated by choice of several characteristics [*cf.* W.B. Russel, *Colloidal Dispersions*, (Cambridge University Press, Cambridge, England, 1991)]:

(A) Radius and material of "solid" core

(B) Solvent composition, including ionic strength

(C) Attachment of functional groups to colloid surface

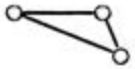
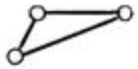
(D) Control of temperature and colloid concentration

(E) Application of rapidly rotating electric field (two dimensional systems)

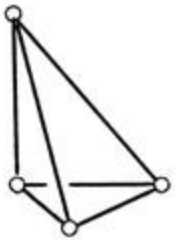
POSSIBLE *vs.* IMPOSSIBLE TARGETS WITH ISOTROPIC PAIR POTENTIALS

- Isotropic pair potentials $\mathbf{v}_2(r)$ produce exactly the same overall potential energy for chiral (mirror image) pairs of structures.

One dimension: *vs.*

Two dimensions:  *vs.* 

Three dimensions:

vs. 

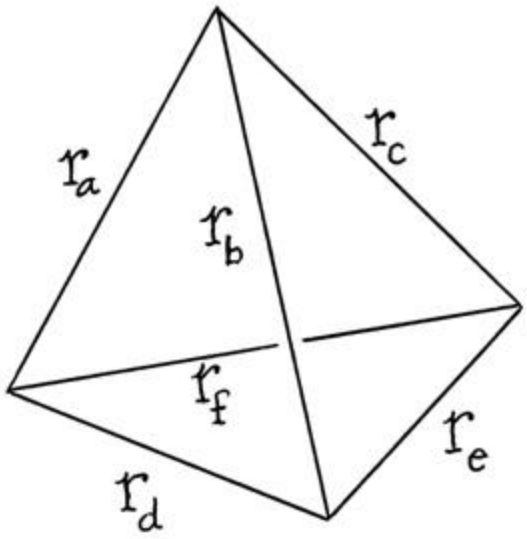
- This potential energy degeneracy persists even when three-body interactions $\mathbf{v}_3(r,s,t)$ depending only on scalar distances are included.

TETRAHEDRON AMBIGUITY

Consider six distinguishable pair distances ("sticks"):

$$r_a < r_b < r_c < r_d < r_e < r_f \quad .$$

If r_f is not too much larger than r_a, these sticks can be assembled in three dimensions any order to form a tetrahedron. Three sticks emanate from each of the four tetrahedron vertices, *e.g.*:



Total number of distinct tetrahedra: $6!/(4 \cdot 3) = 60$. These occur in pairs as mirror images of one another.

The sum of isotropic pair potentials is the same for all 60 isomers.

LATTICE SUMS

- Crystal structures can be characterized by coordination shell distances r_n and occupancies Z_n.

- Potential energy per particle for isotropic pair potential $v_2(r)$:

$$\Phi / N = (1/2) \sum_{n=1}^{\infty} Z_n v_2(r_n) \ .$$

- Representative coordination patterns ("structural fingerprints"):

	SC	BCC	FCC
$(r_1/r_1)^2$	1	1	1
Z_1	6	8	12
$(r_2/r_1)^2$	2	4/3	2
Z_2	12	6	6
$(r_3/r_1)^2$	3	8/3	3
Z_3	8	12	24
$(r_4/r_1)^2$	4	11/3	4
Z_4	6	24	12
$(r_5/r_1)^2$	5	4	5
Z_5	24	8	24

- Impossible to examine all possible periodic structures, but a limited search can be a useful $v_2(r)$ "filter".

NECESSARY CONDITIONS FOR $v_2(r)$

- $v_2(r)$ should be continuous and at least twice differentiable for distances beyond a hard core (if any).
- Lattice sum must indicate positive-pressure stability range compared to other crystal structures tested.
- All phonons must have real frequencies.
- Point defects (vacancies, interstitials) must have positive energies of creation.
- Computer simulation (MC, MD) starting with high temperature fluid should reproducibly exhibit spontaneous self-assembly of target structure upon cooling toward T=0.
- Energy scaling: equilibrium melting point should have $k_B T_m \approx 1$.
- Distance scaling: nearest neighbor distance in crystal should be $r_1 \approx 1$.

LENNARD-JONES PAIR POTENTIAL

- $v_{LJ}(r) = 4\varepsilon[(\sigma/r)^{12} - (\sigma/r)^{6}]$
- ε, σ set the energy and length scales.
- $v_{LJ}(r)$ exhibits a single minimum at $r = 2^{1/6}\sigma$, with depth $-\varepsilon$.
- The classical ground-state structure in two dimensions is the perfect triangular (close-packed) crystal at all non-negative pressures.
- Published papers often assume the classical ground state for $v_{LJ}(r)$ in three dimensions is the face-centered cubic (FCC) crystal. But it was shown long ago that the ground state is a hexagonal close-packed (HCP) crystal except at extremely high pressures [T. Kihara and S. Koba, J. Phys. Soc. Jpn. 7, 348 (1952)].
- However *Ar*, *Kr*, and *Xe* are face-centered cubic at ordinary pressures!
- Shortest distance distinction between FCC and HCP occurs in the third coordination shell.

  FCC: $(r_3/r_1)^2 = 3$, $Z_3 = 24$;

  HCP: $(r_3/r_1)^2 = 8/3$, $Z_3 = 2$.

  Make $v_2(r) > v_{LJ}(r)$ around $r = (8/3)^{1/2} r_1$ to favor FCC.

OPTIMIZATION/SELECTION PROCEDURE

- Select parameterized function set $v_2(r \mid \alpha_1 \ldots \alpha_n)$ covering desired gross features necessary for chosen target structure.

- Typical input components for parameterized function:

$$\alpha_1 / r^{\alpha_2}, \quad \alpha_3 \exp(-\alpha_4 r), \quad \alpha_5 \exp[-\alpha_6 (r - \alpha_7)^2], \quad \frac{\alpha_8}{1 + \alpha_9 \exp(-\alpha_{10} r)} \quad .$$

- Perform lattice sums for target structure and group of competitors. Identify parameter sets that stabilize target over some density (pressure) range.

- Examine phonon spectrum over entire Brillouin zone to assure that no unstable modes exist. Avoid $\alpha_1 \ldots \alpha_n$ sets that yield "soft" modes, if possible.

- Check that point defects (vacancies, interstitials) have positive excitation energies.

- Carry out several multi-particle MC or MD simulations of cooling from high-temperature liquid through freezing point to verify spontaneous assembly in target structure. If defects are frozen in, check that energy lies above lattice sum for target. Try annealing.

- Return to beginning?

SQUARE LATTICE

[M. Rechtsman, F. Stillinger, and S. Torquato, Phys. Rev. E **73**, 011406 (2006)]

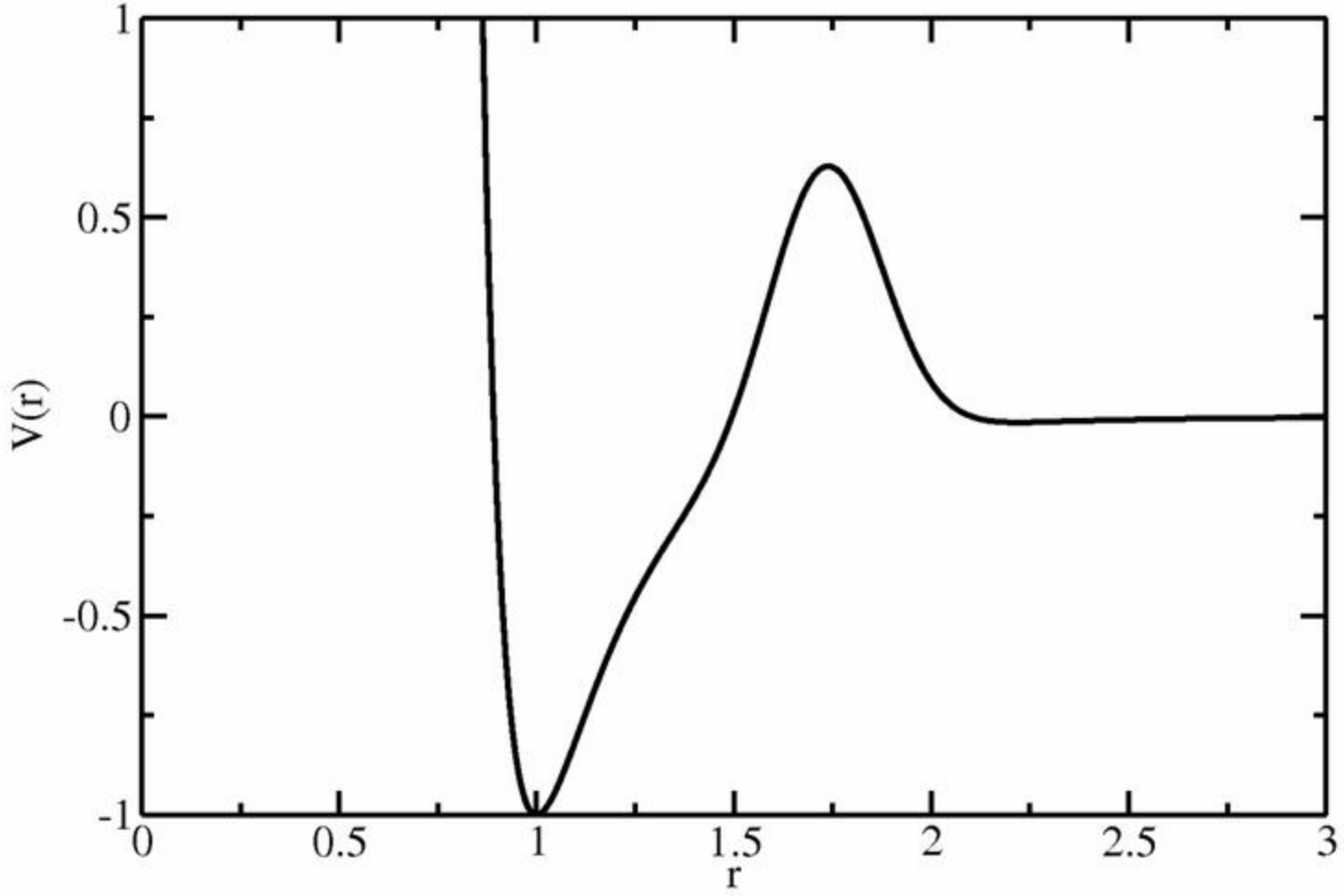
- Coordination shell is distinct from triangular (close-packed) lattice:

	$\left(\frac{r_1}{r_1}\right)^2$	Z_1	$\left(\frac{r_2}{r_1}\right)^2$	Z_2	$\left(\frac{r_3}{r_1}\right)^2$	Z_3	$\left(\frac{r_4}{r_1}\right)^2$	Z_4
SQ:	1	4	2	4	4	4	5	8
TRI:	1	6	3	6	4	6	7	12

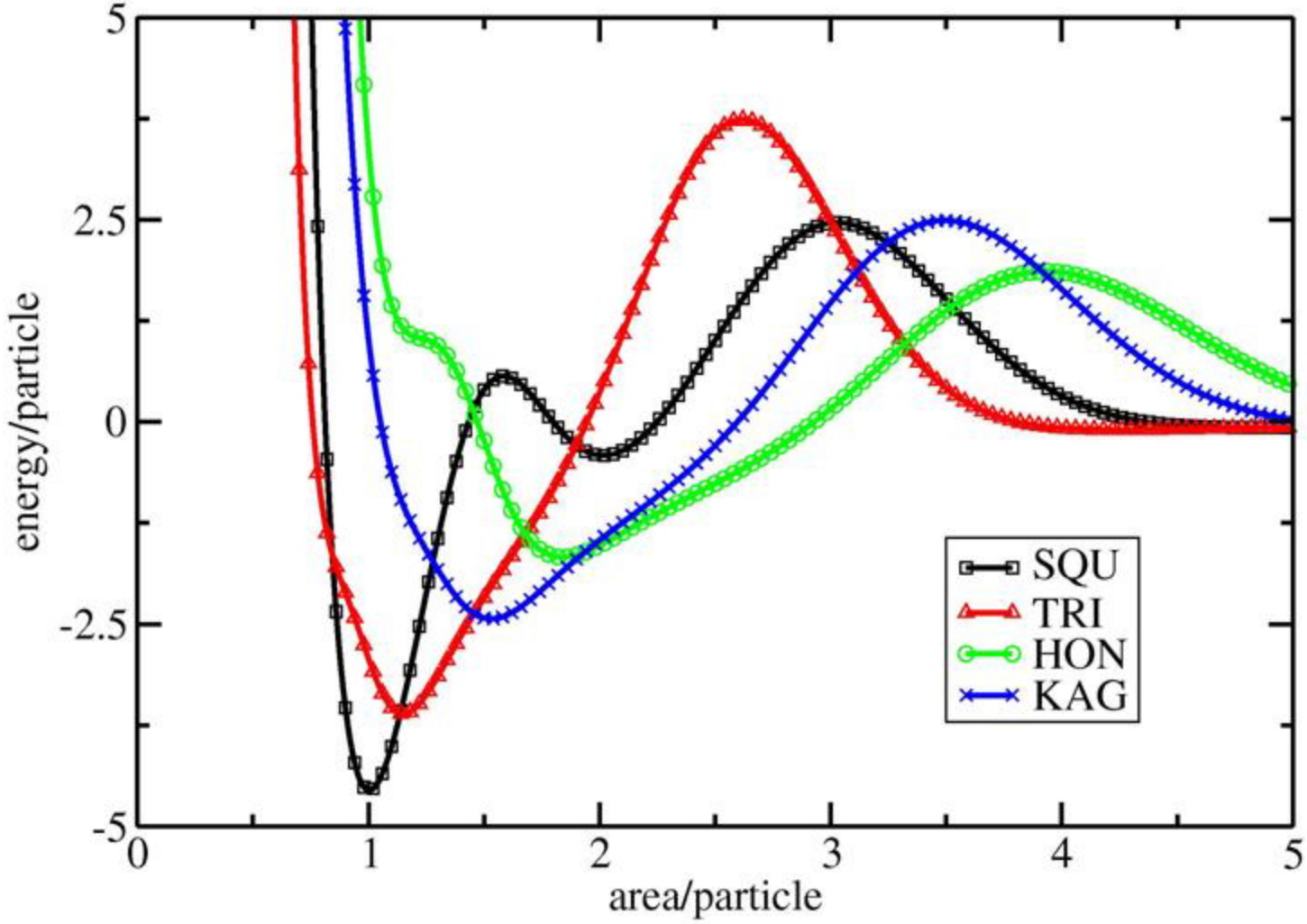
- Necessary to penalize occurrence of more than 4 nearest neighbors.

- Reward occurrence of pairs at distances $2^{1/2}r_1$ and $5^{1/2}r_1$.

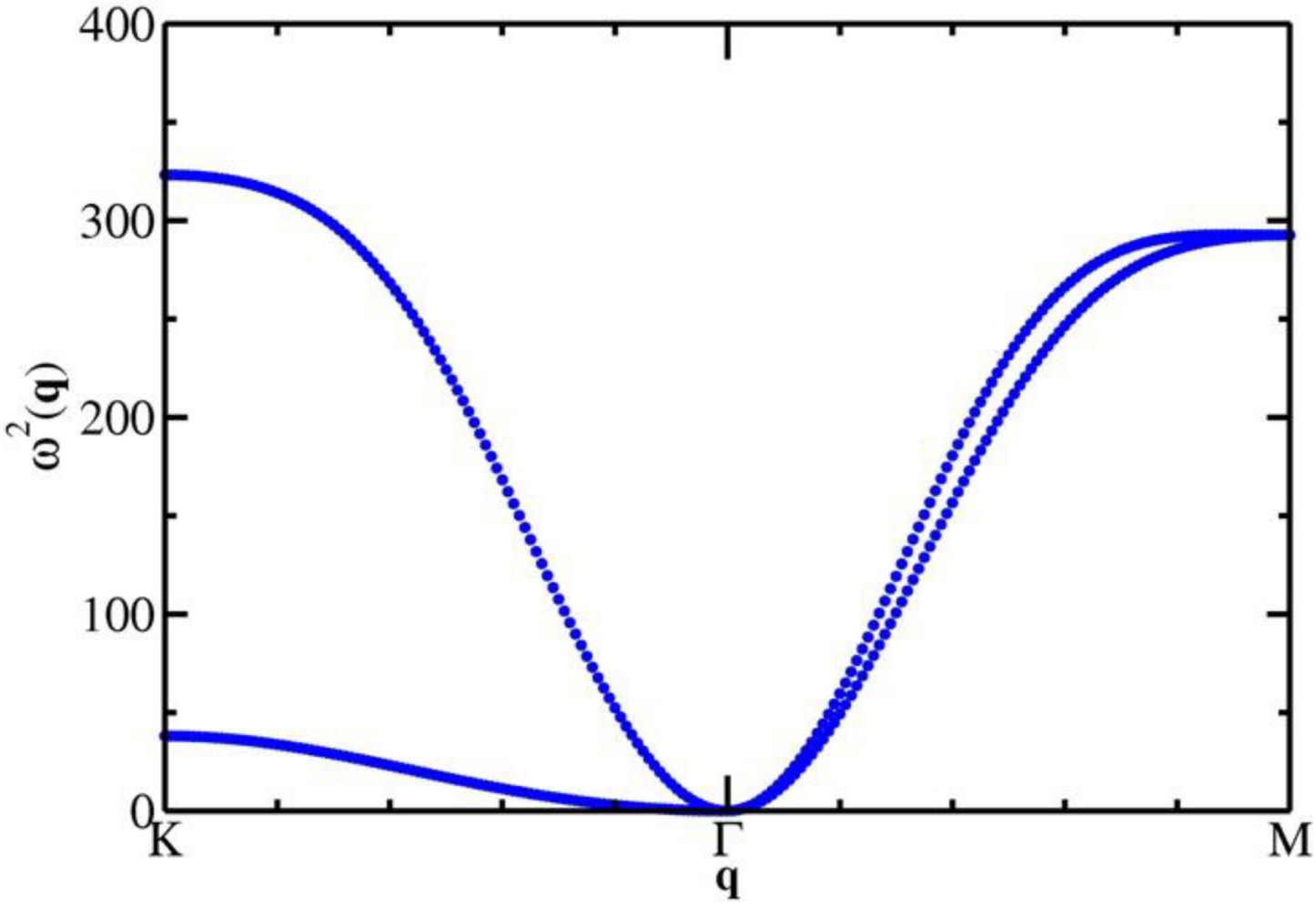
Square lattice potential



Square lattice sums



Square lattice phonon spectrum



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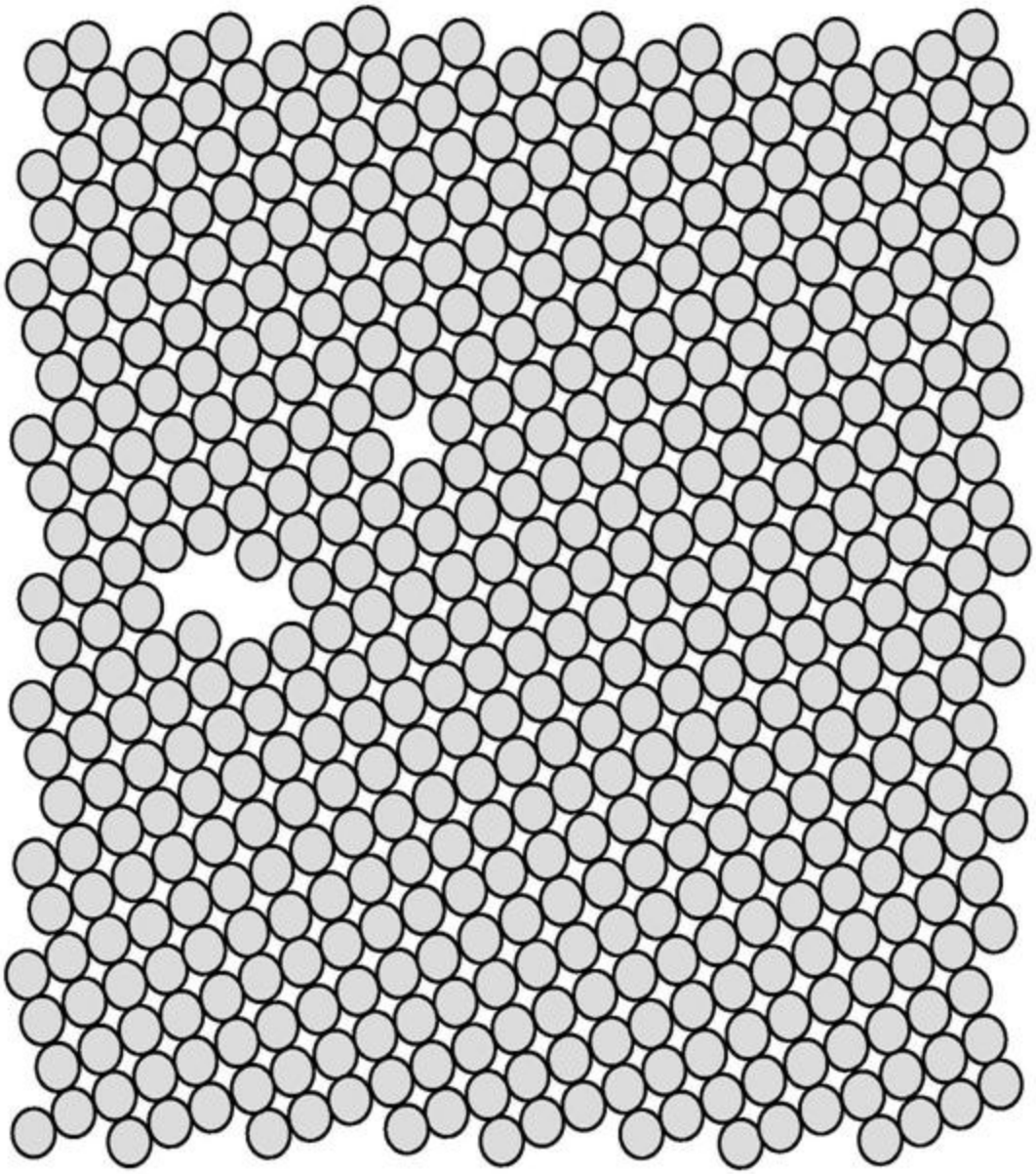
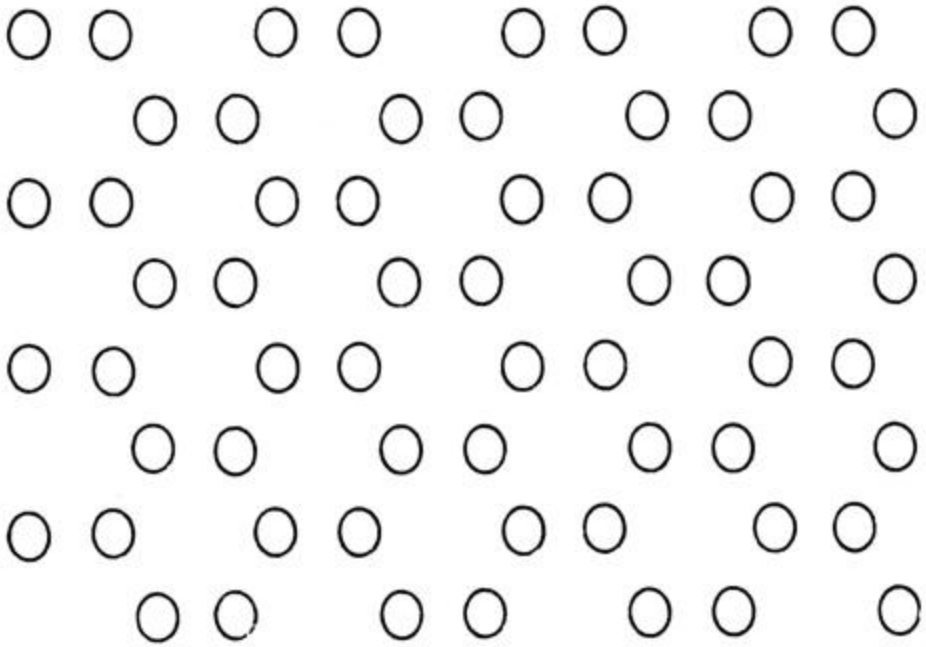
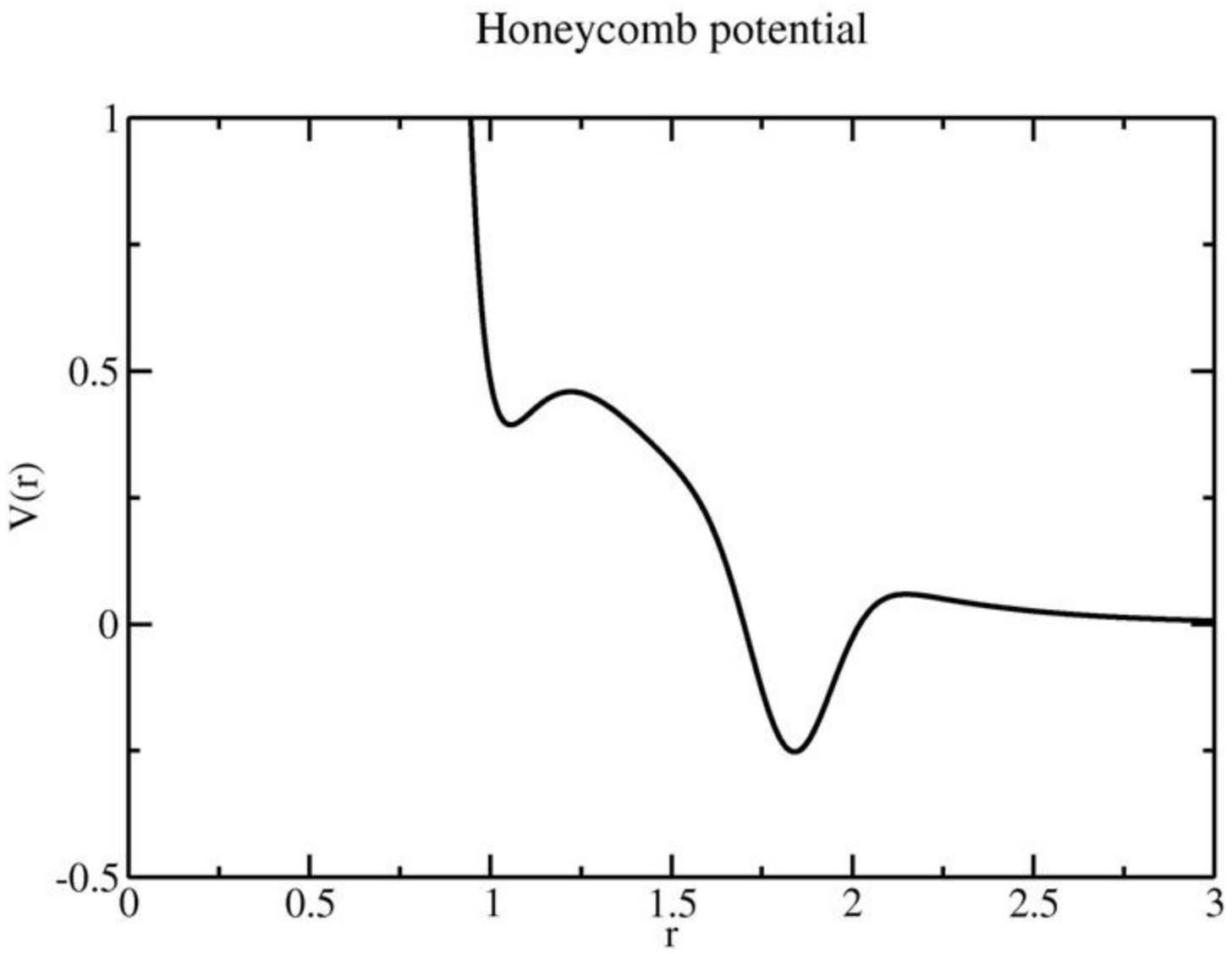
squ-mc



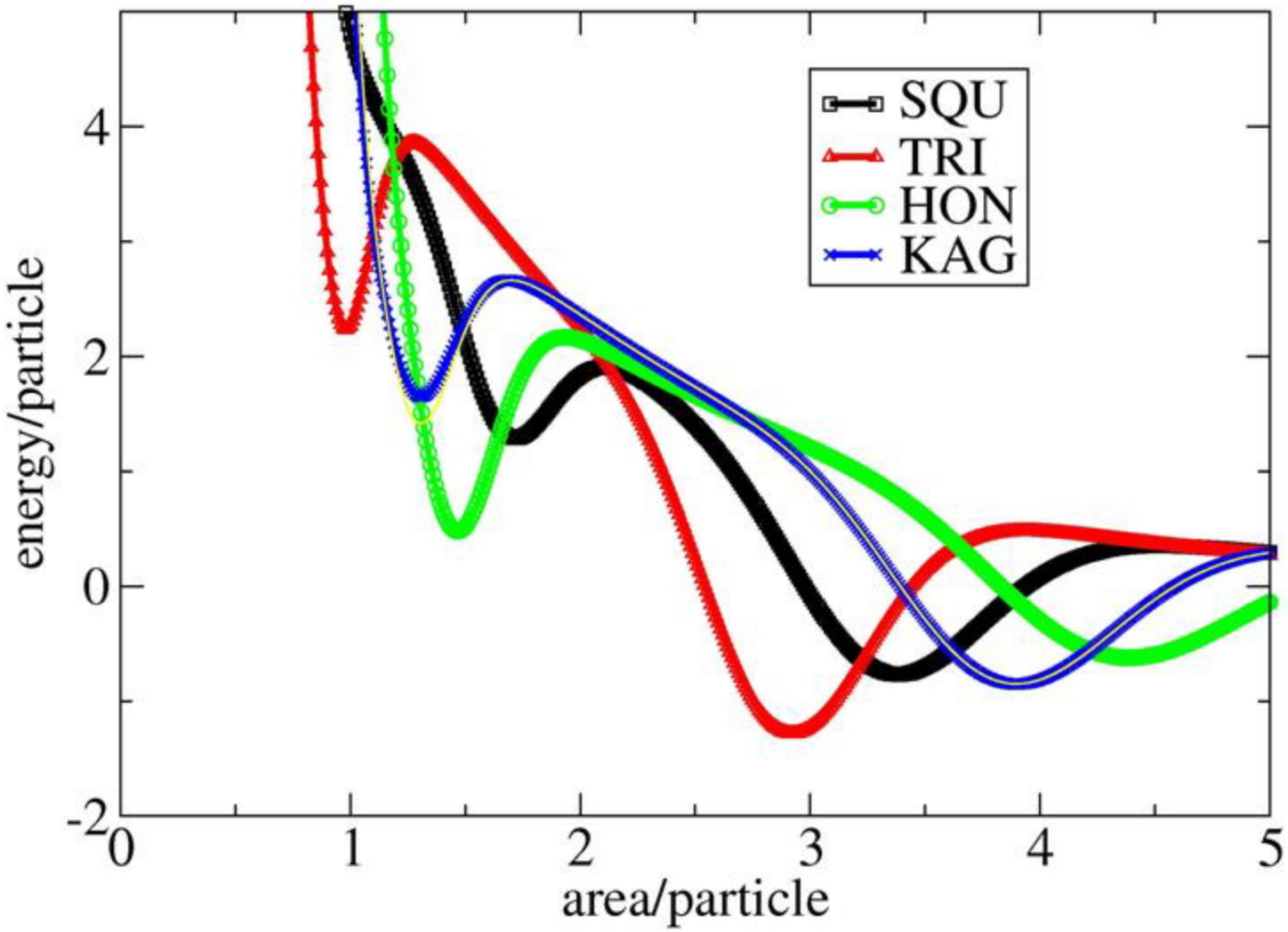
TWO-DIMENSIONAL HONEYCOMB CRYSTAL



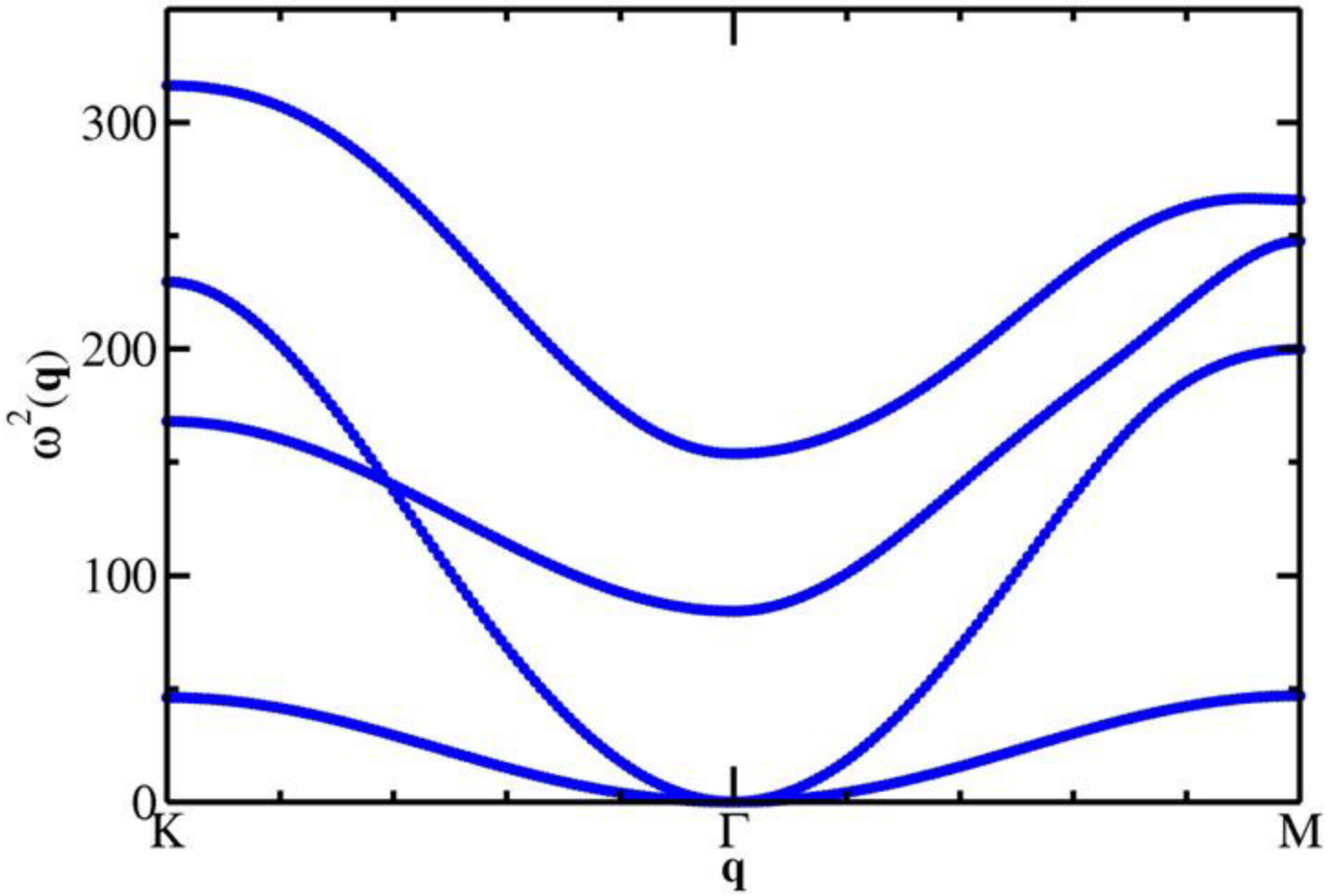
- Open structure, all particles three-fold coordinated.
- Periodic unit cell contains two particles.
- Formed by removing 1/3 of particles from close-packed triangular lattice.
- The honeycomb coordination shell relative distances r_n / r_1 are identical to those in the close-packed triangular lattice. However some of the coordination numbers Z_n differ.


Honeycomb potential
1
0.5
0
-0.5
V(r)
0
0.5
1
1.5
2
2.5
3
r

Honeycomb lattice sums



Honeycomb phonon spectrum



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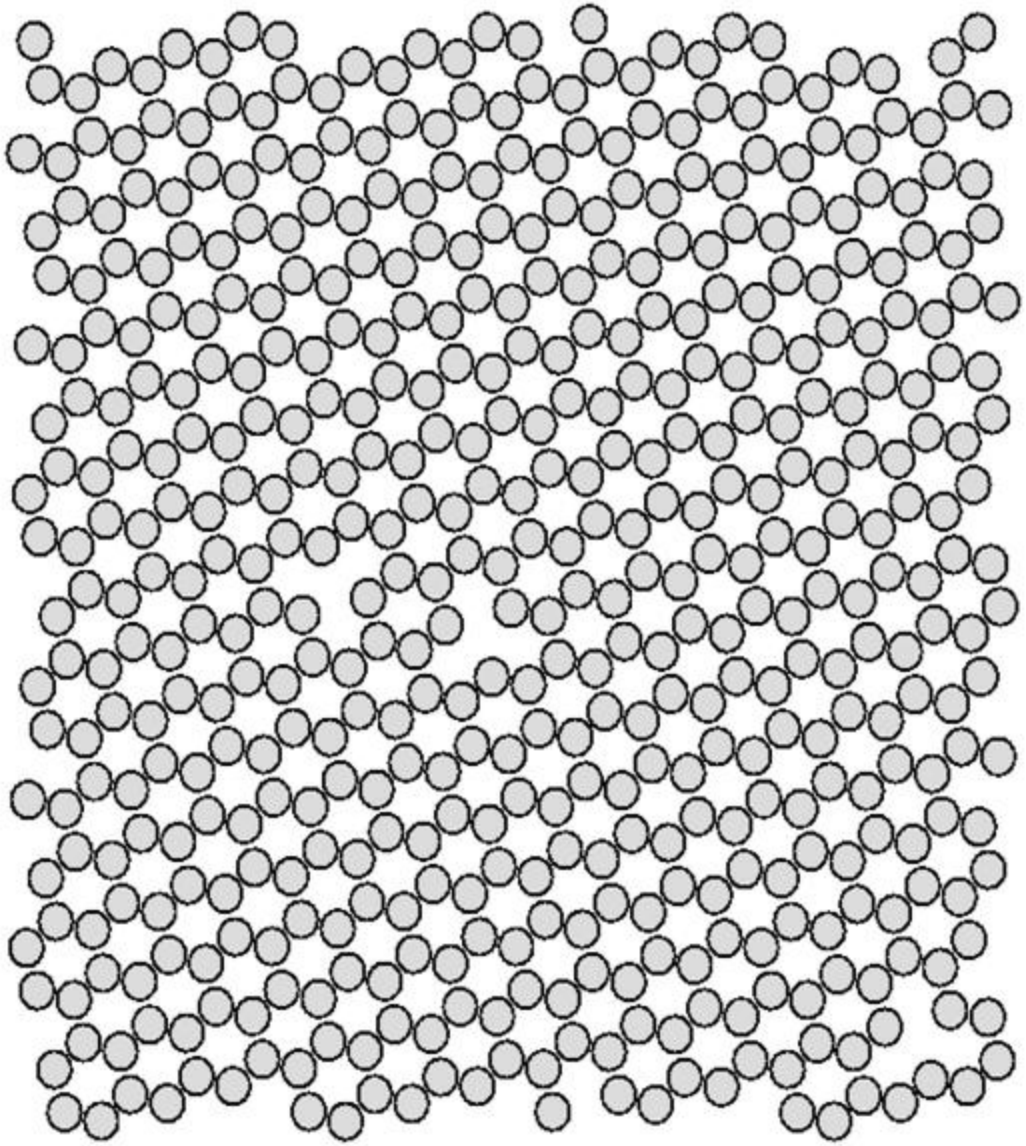
hon-mc



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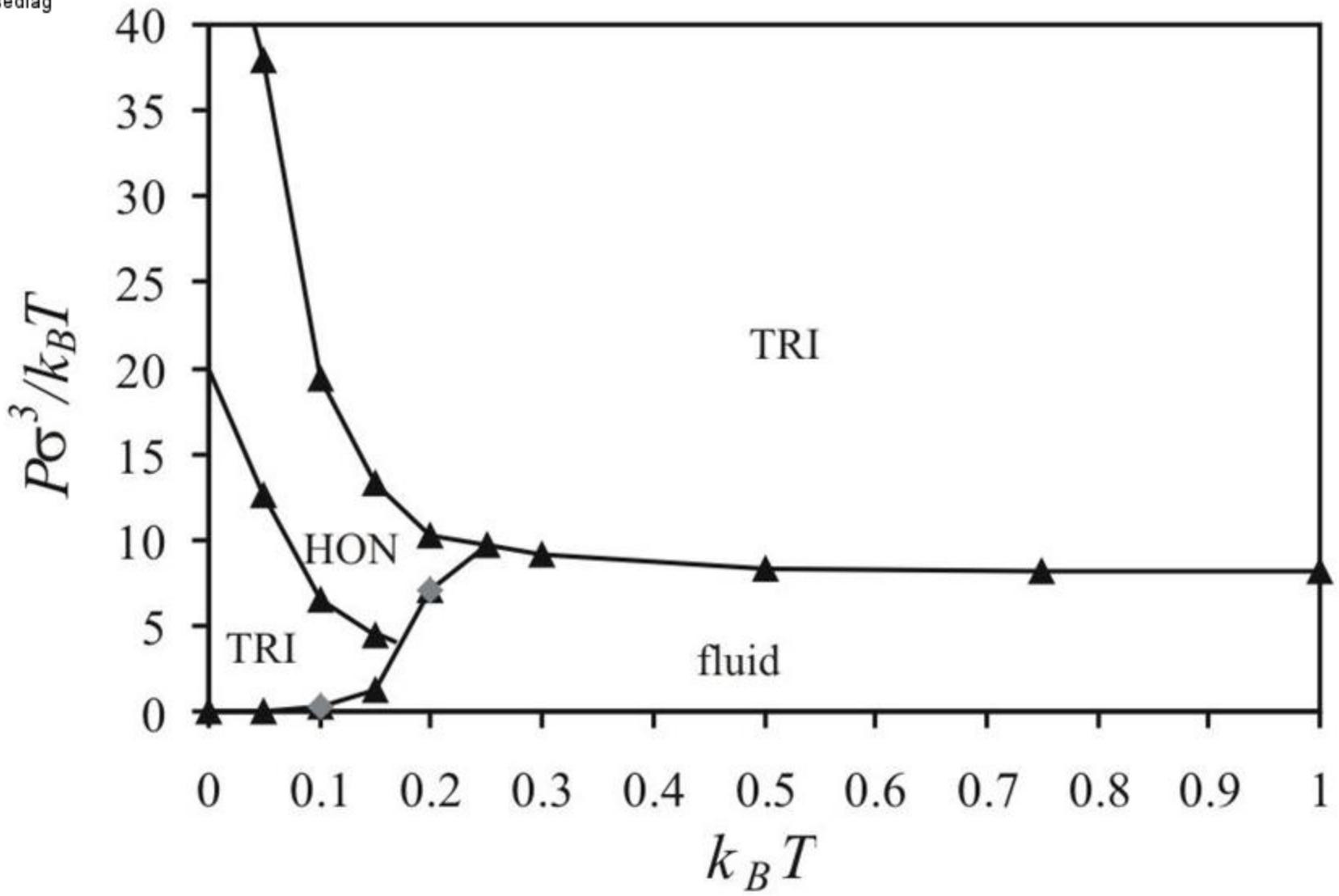
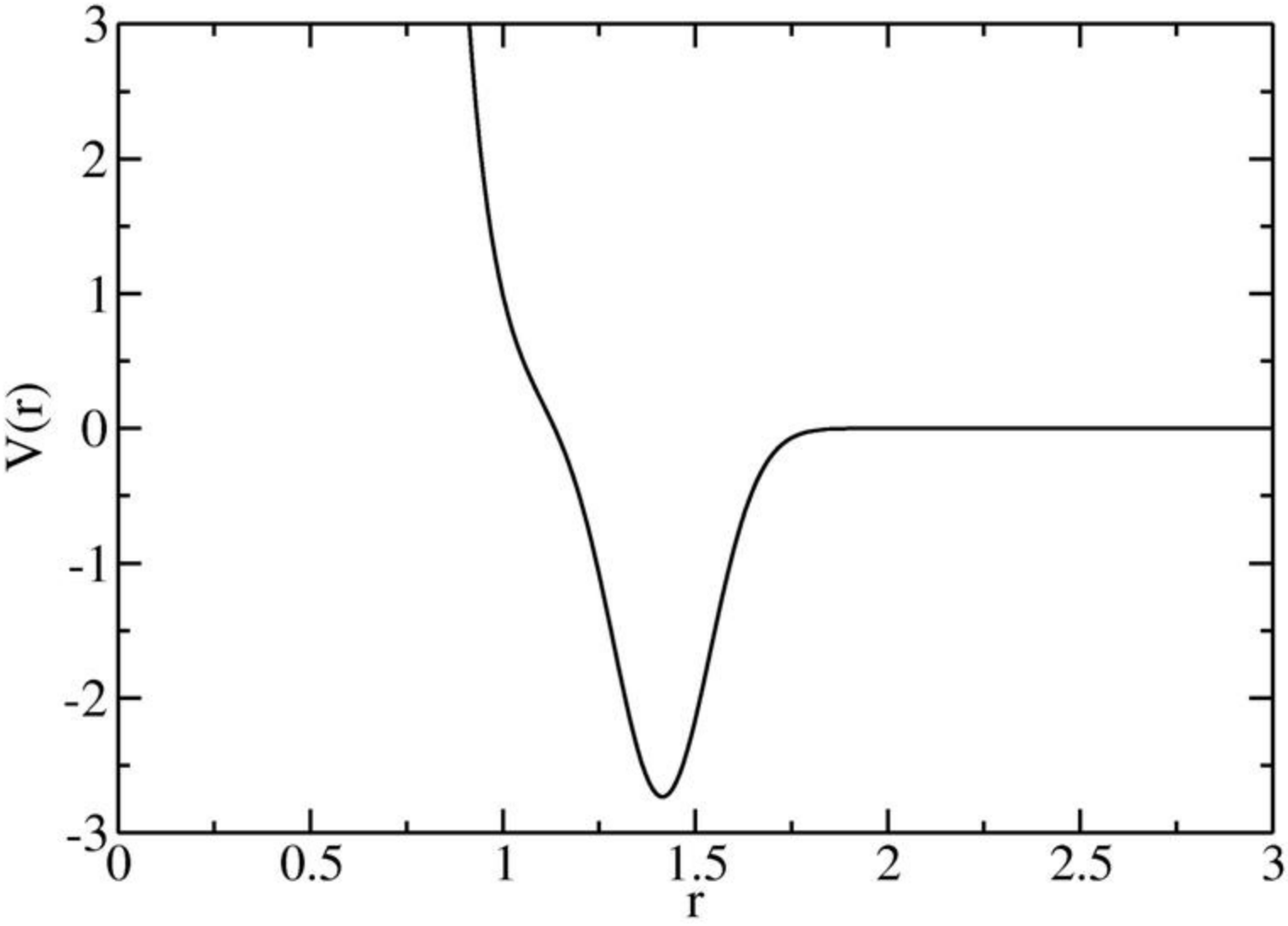
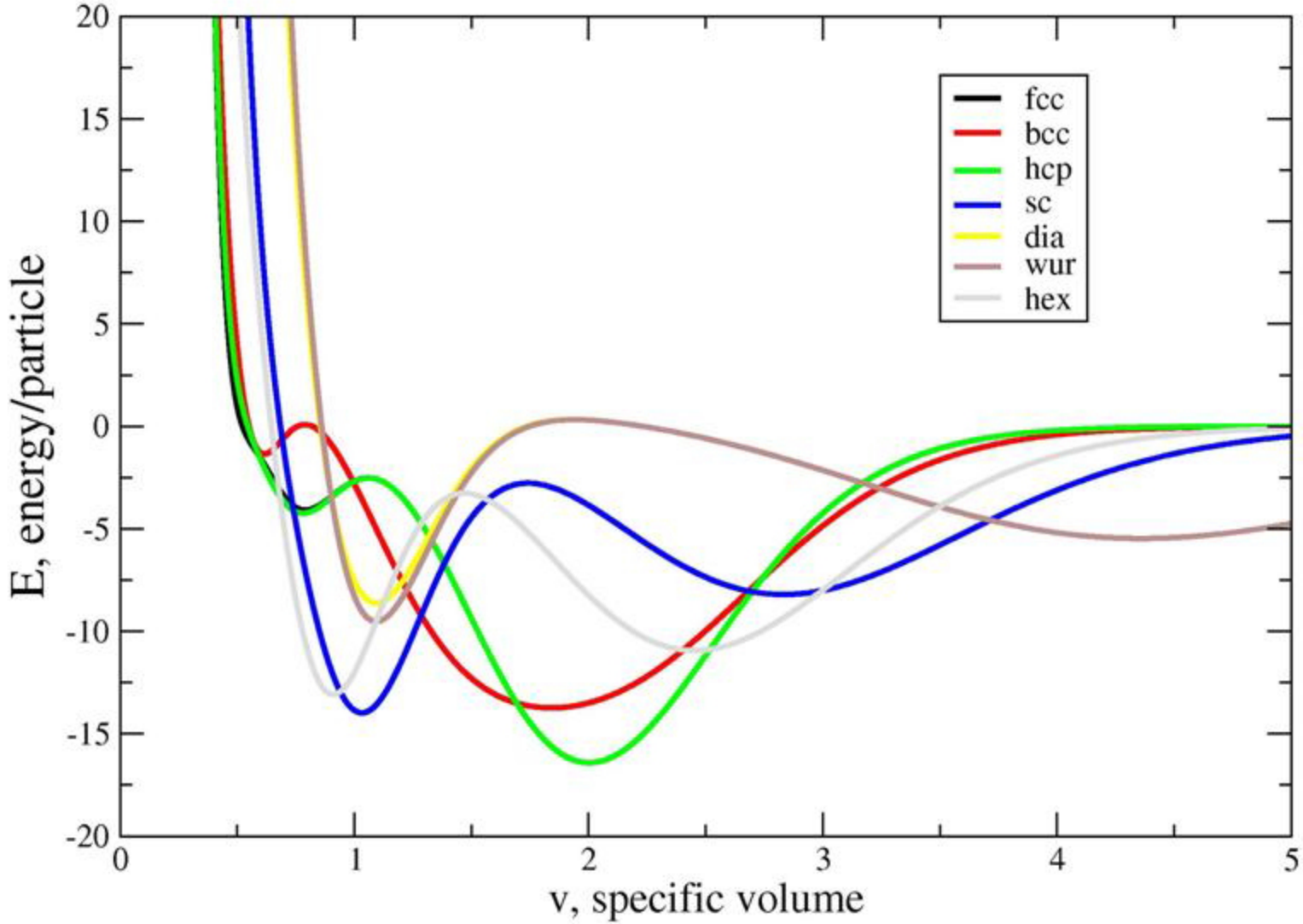
PTphasediag



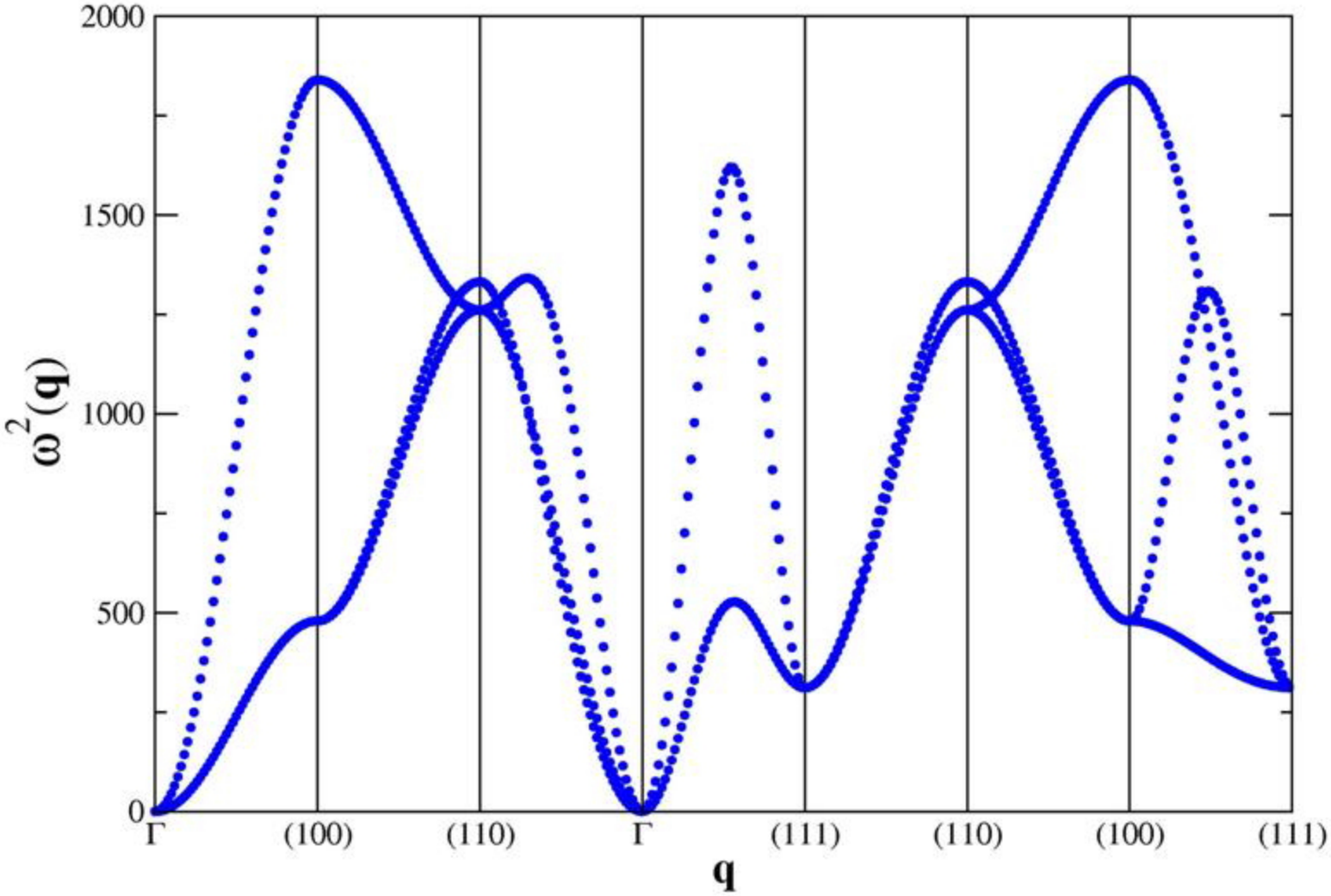
Simple cubic potential



Simple cubic lattice sums



Simple cubic phonon spectrum



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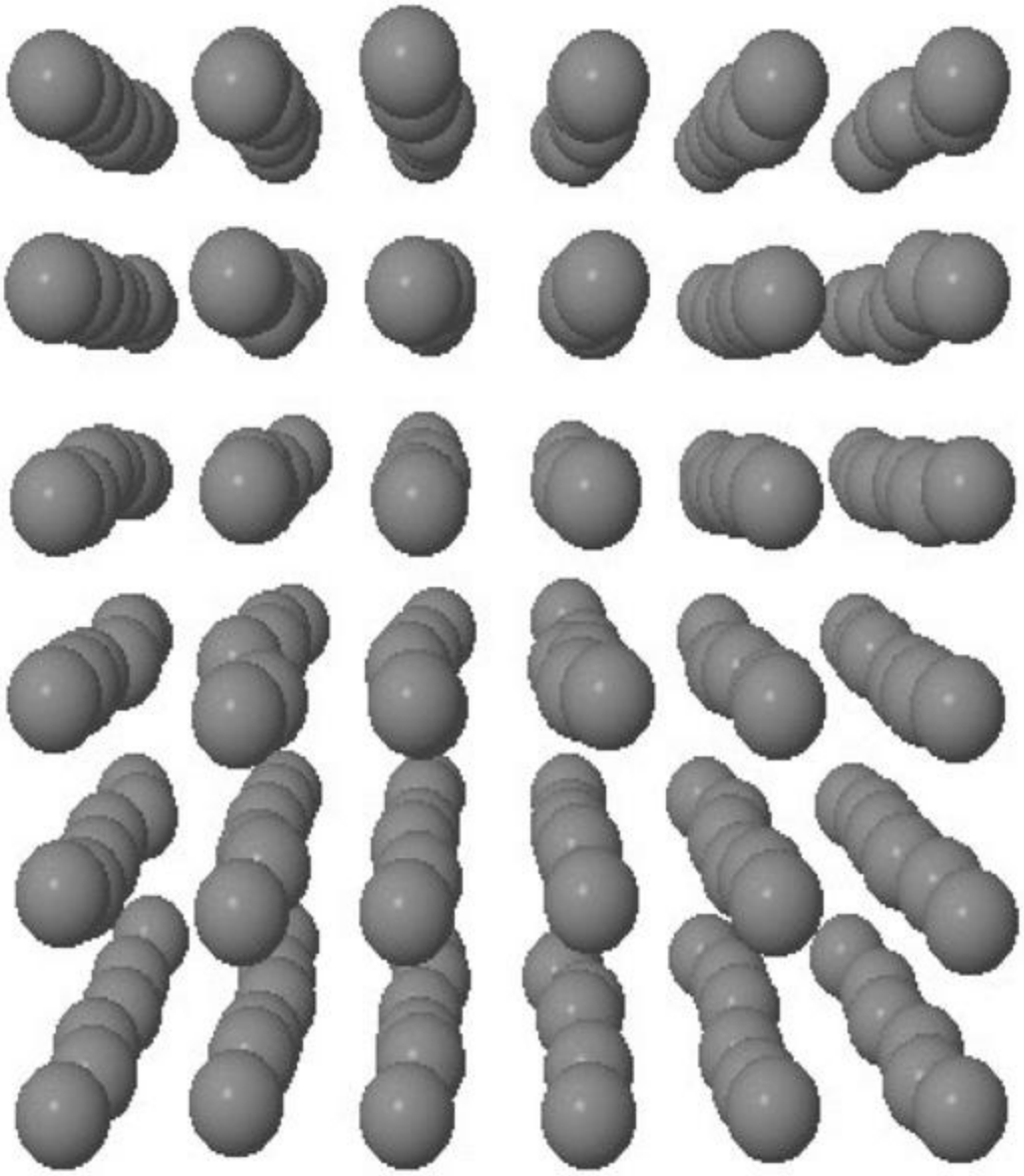
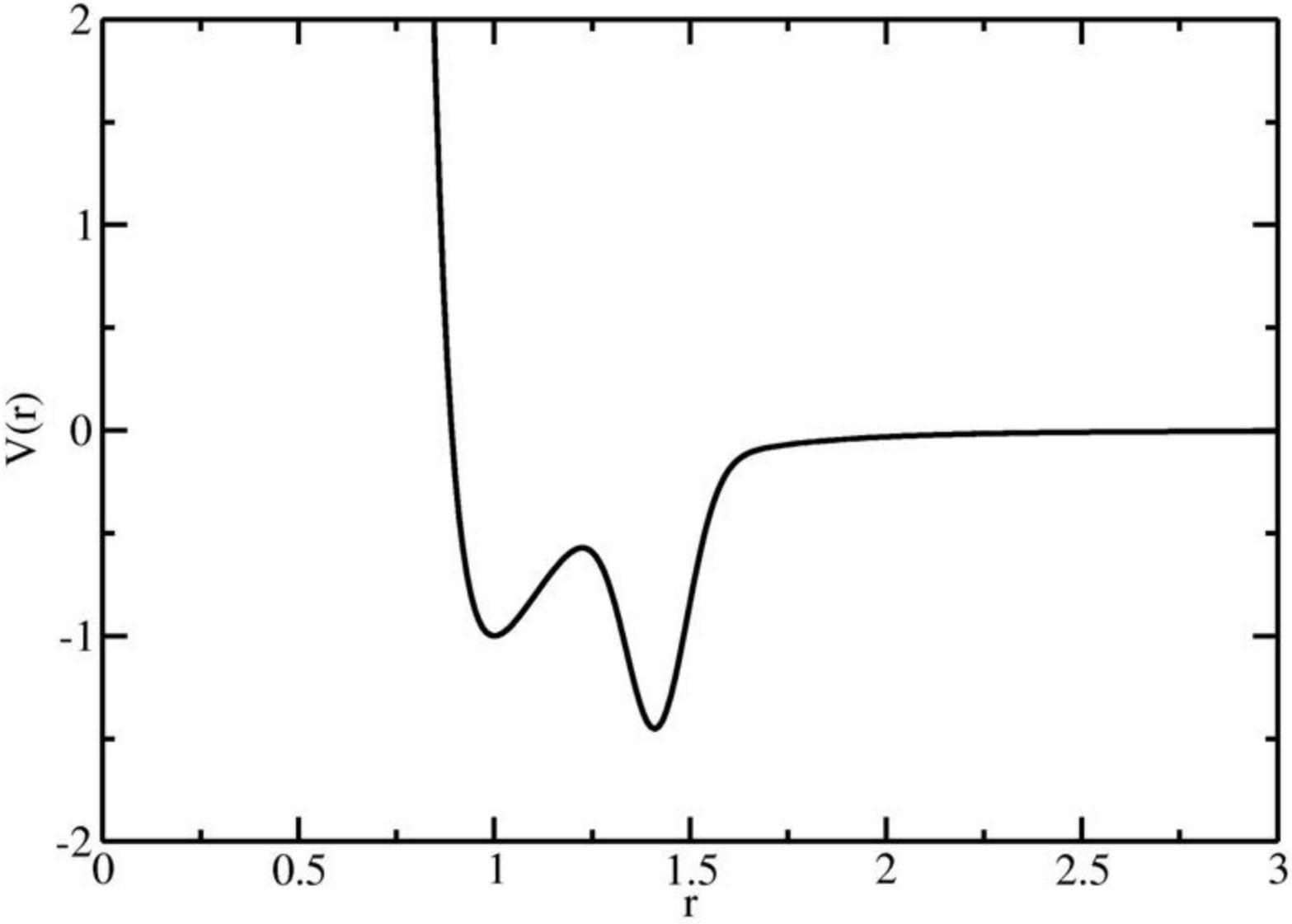
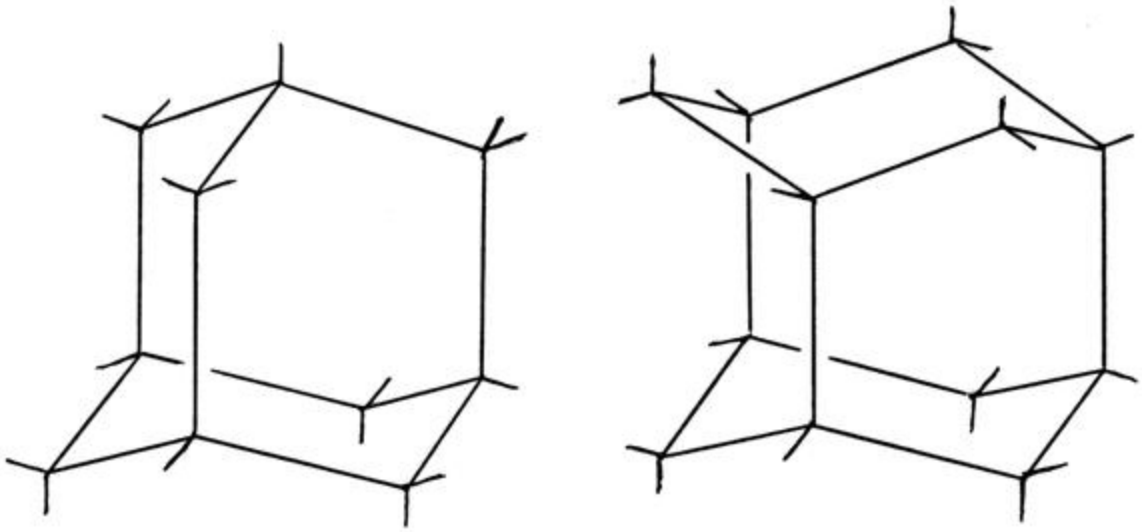
sc-md



Simple hexagonal potential



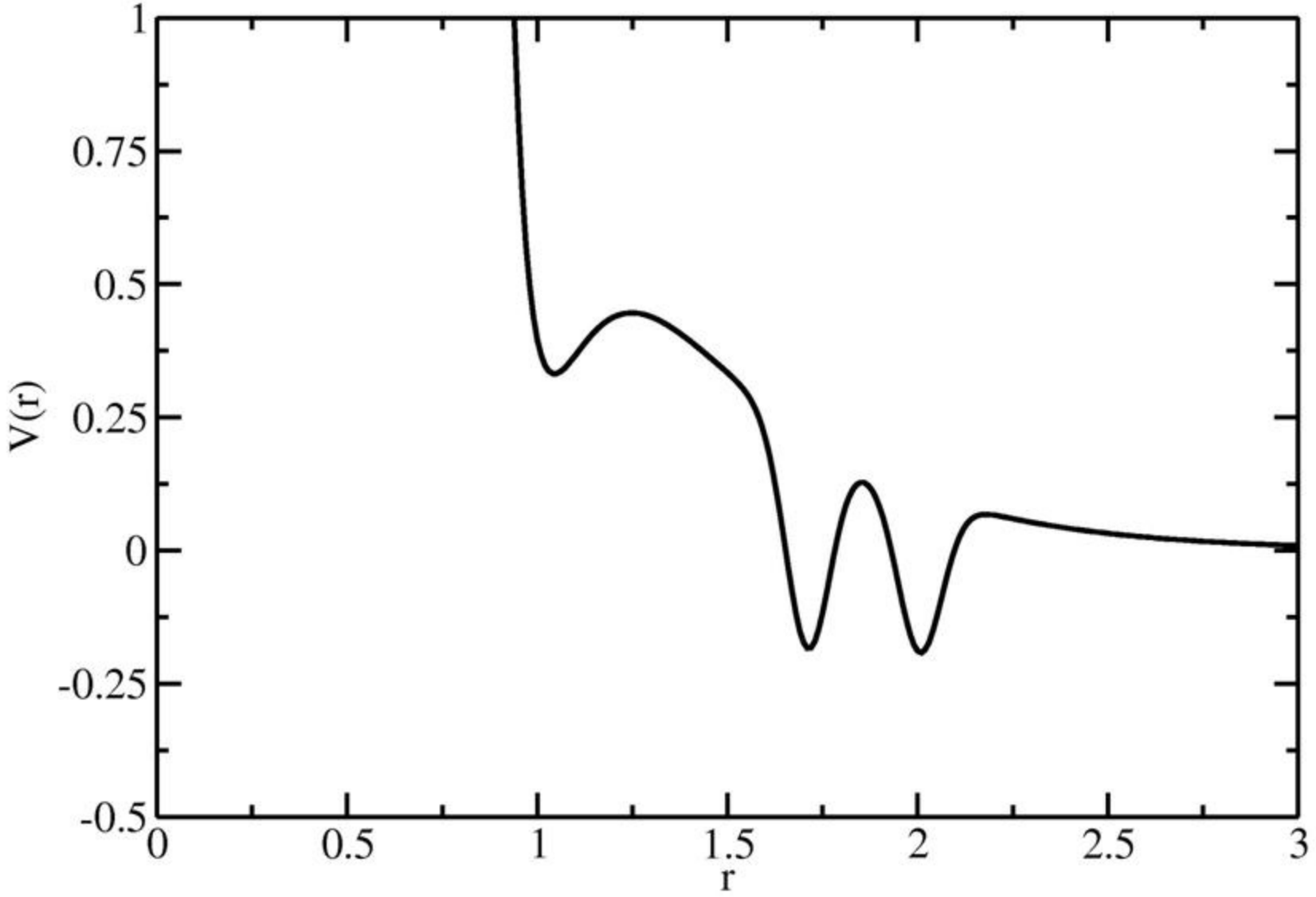
DIAMOND *vs.* WURTZITE STRUCTURES



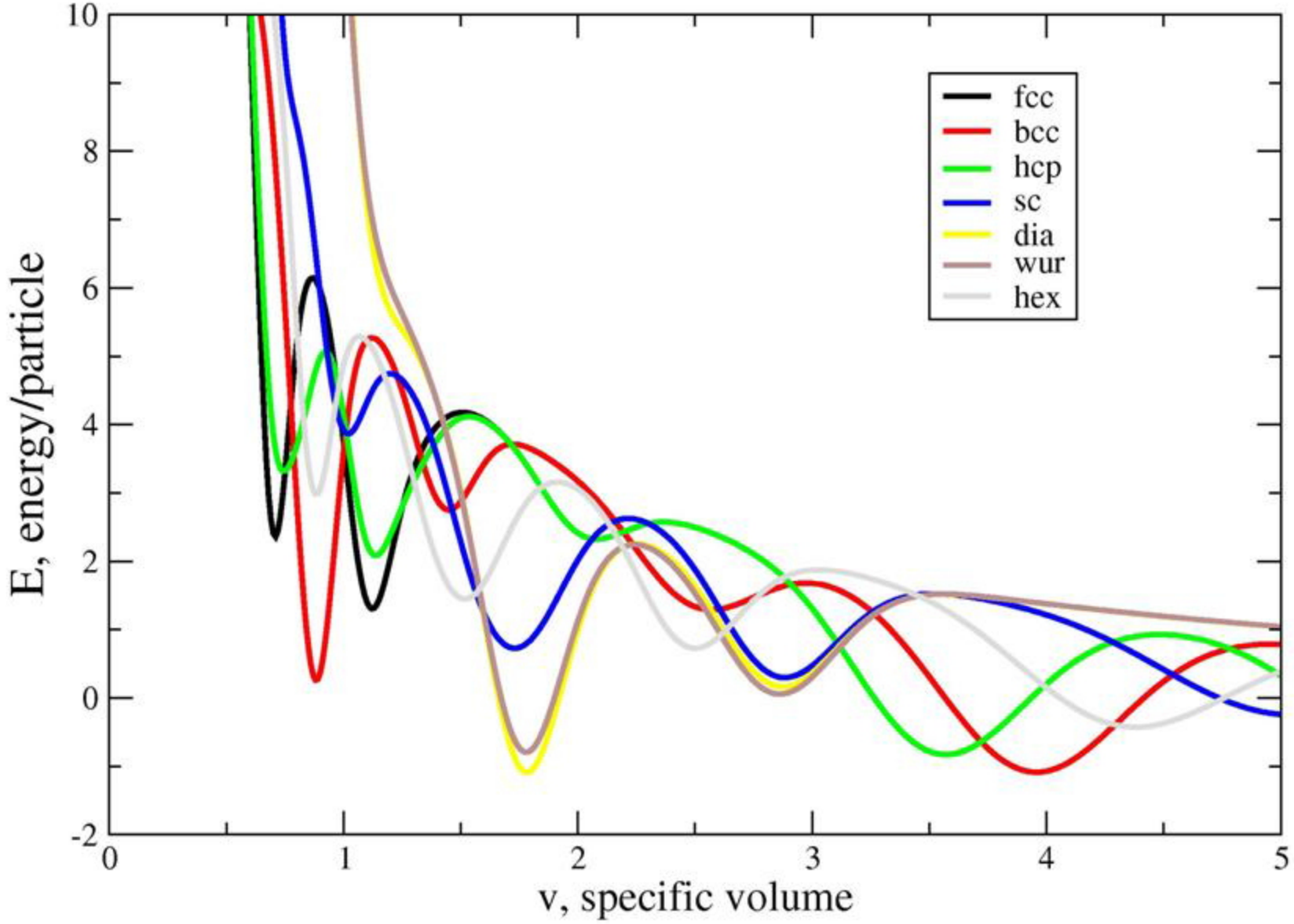
diamond wurtzite

- Both exhibit open structures with four-fold coordination.
- Particles in periodic unit cell: 2 for diamond, 4 for wurtzite.
- Hexagons of nearest-neighbor bonds are all "chair form" in the diamond structure. In the wurtzite structure half are "boat form", and half are "chair form".
- Due to the "boat form", wurtzite has pairs at $r_2 = (5/3)\eta_1$ where diamond has none. This is a discriminating feature useful in devising $v_2(r)$ for one or the other.

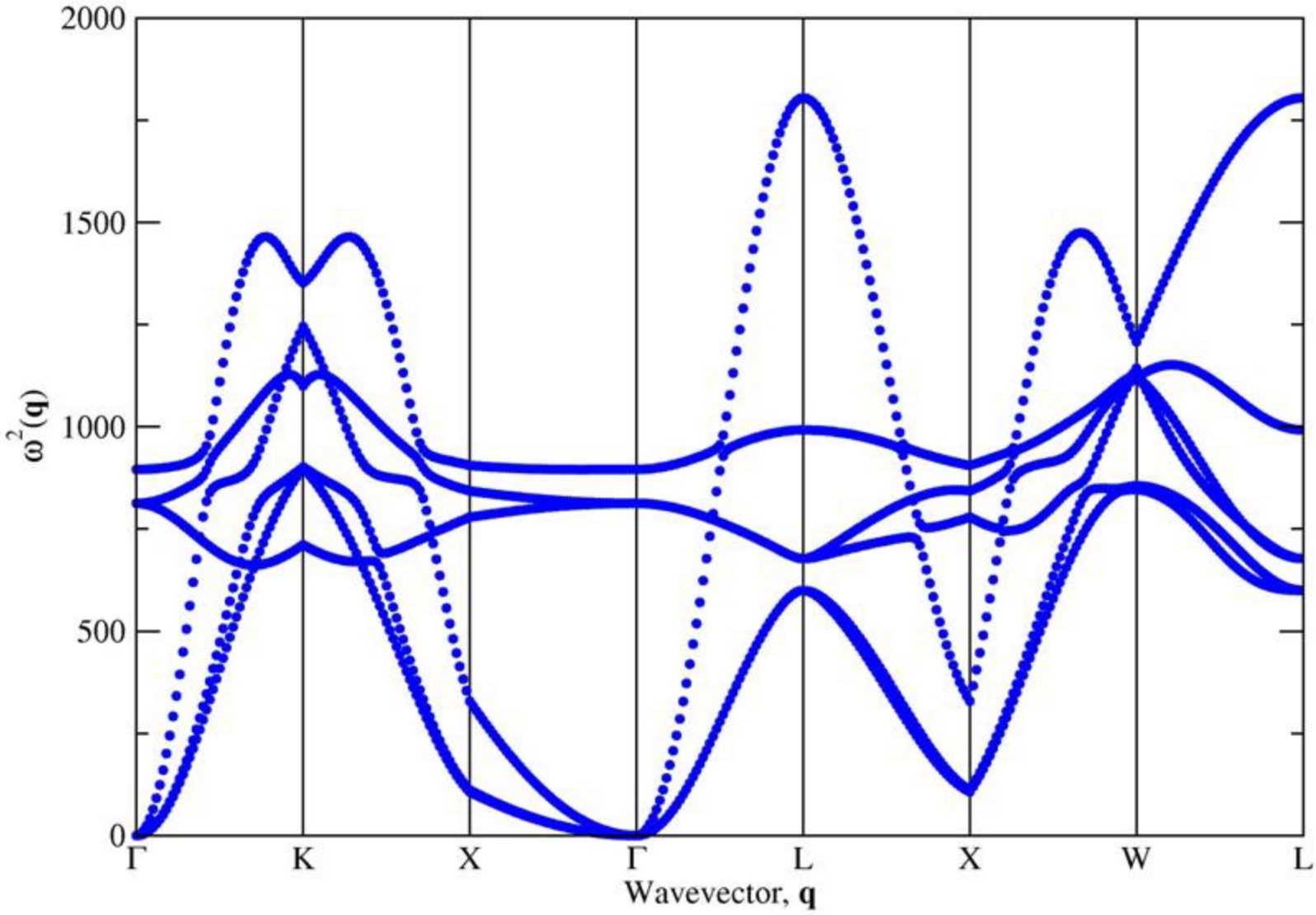
Diamond potential



Diamond lattice sums



Diamond phonon spectrum



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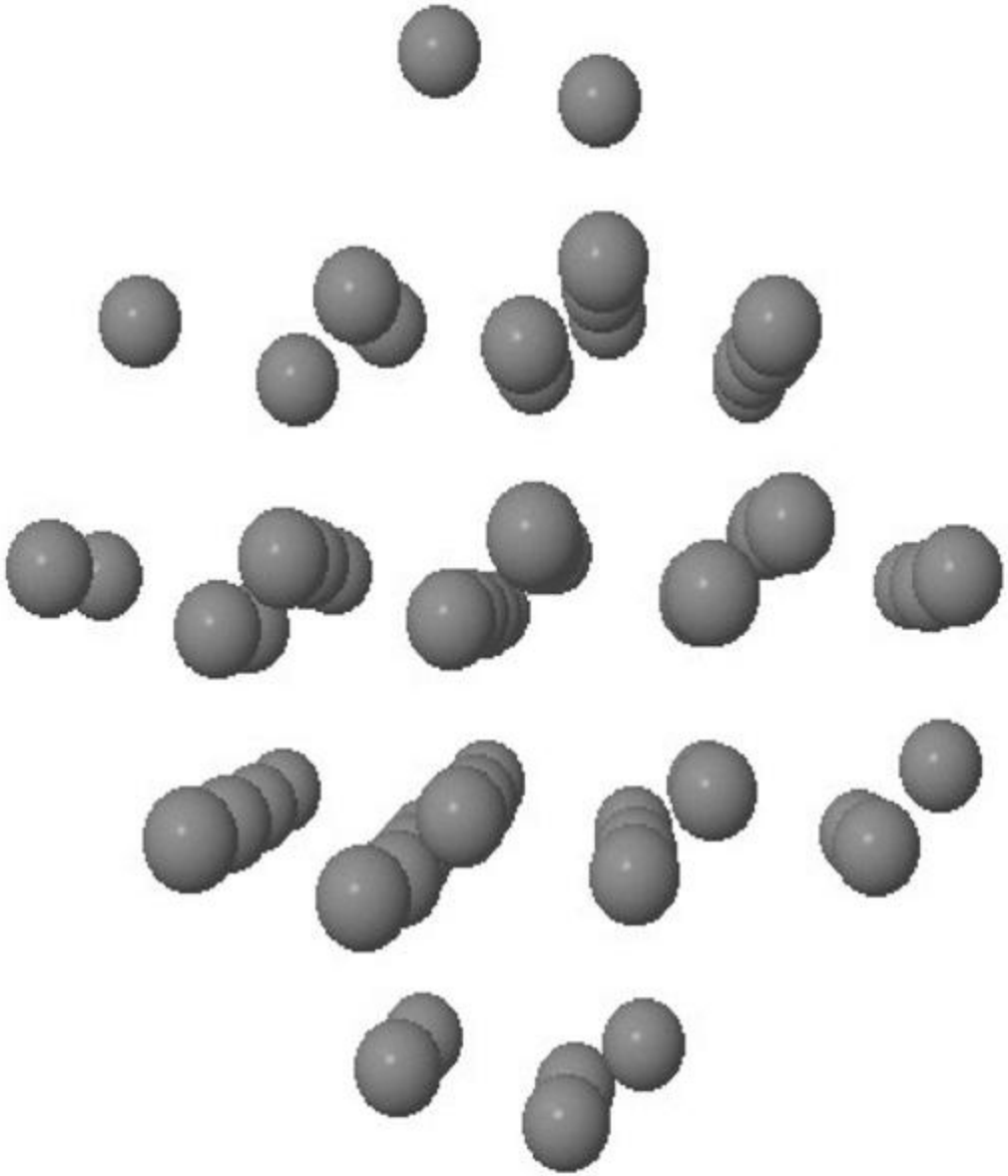
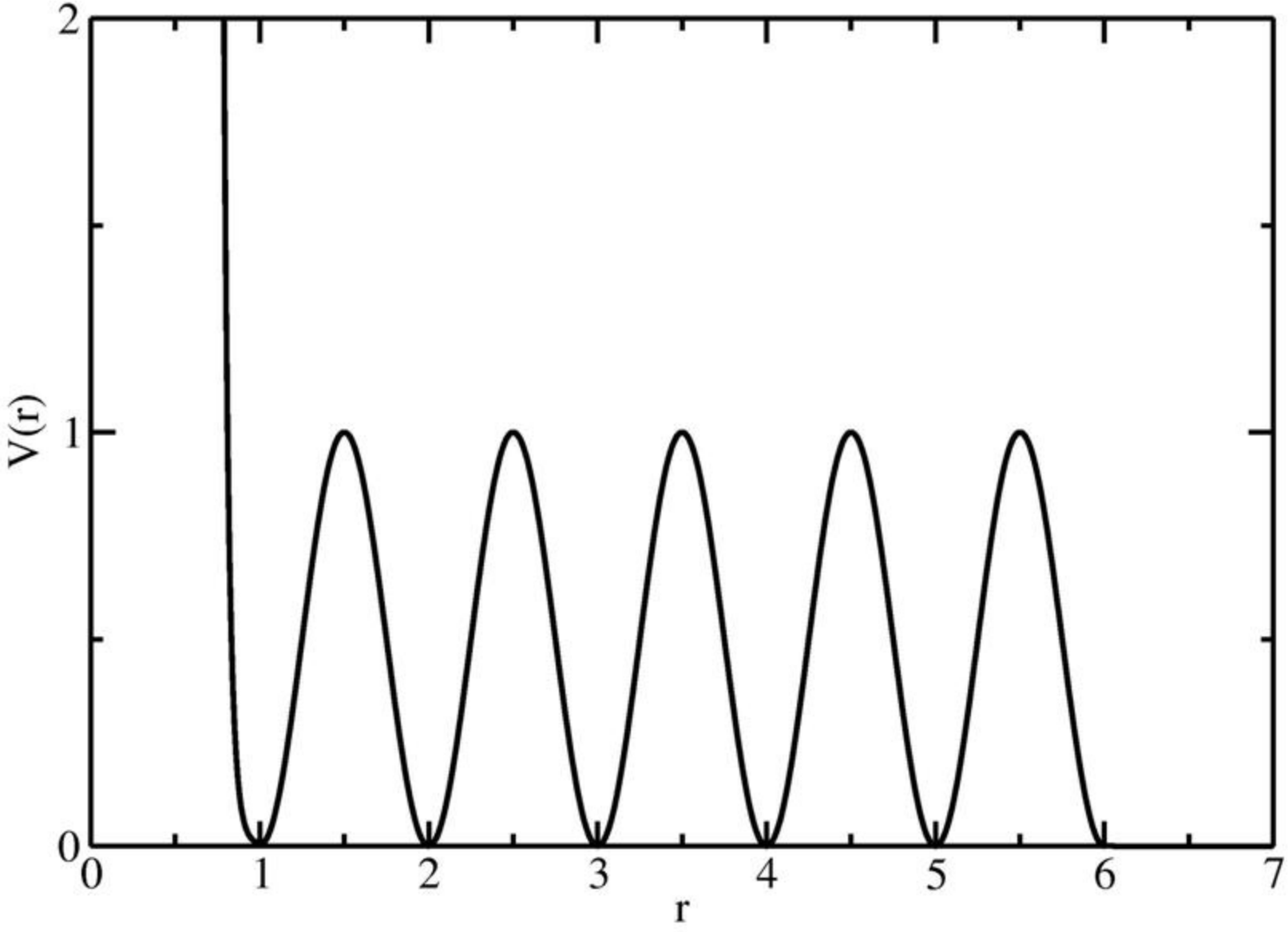


5 finger potential



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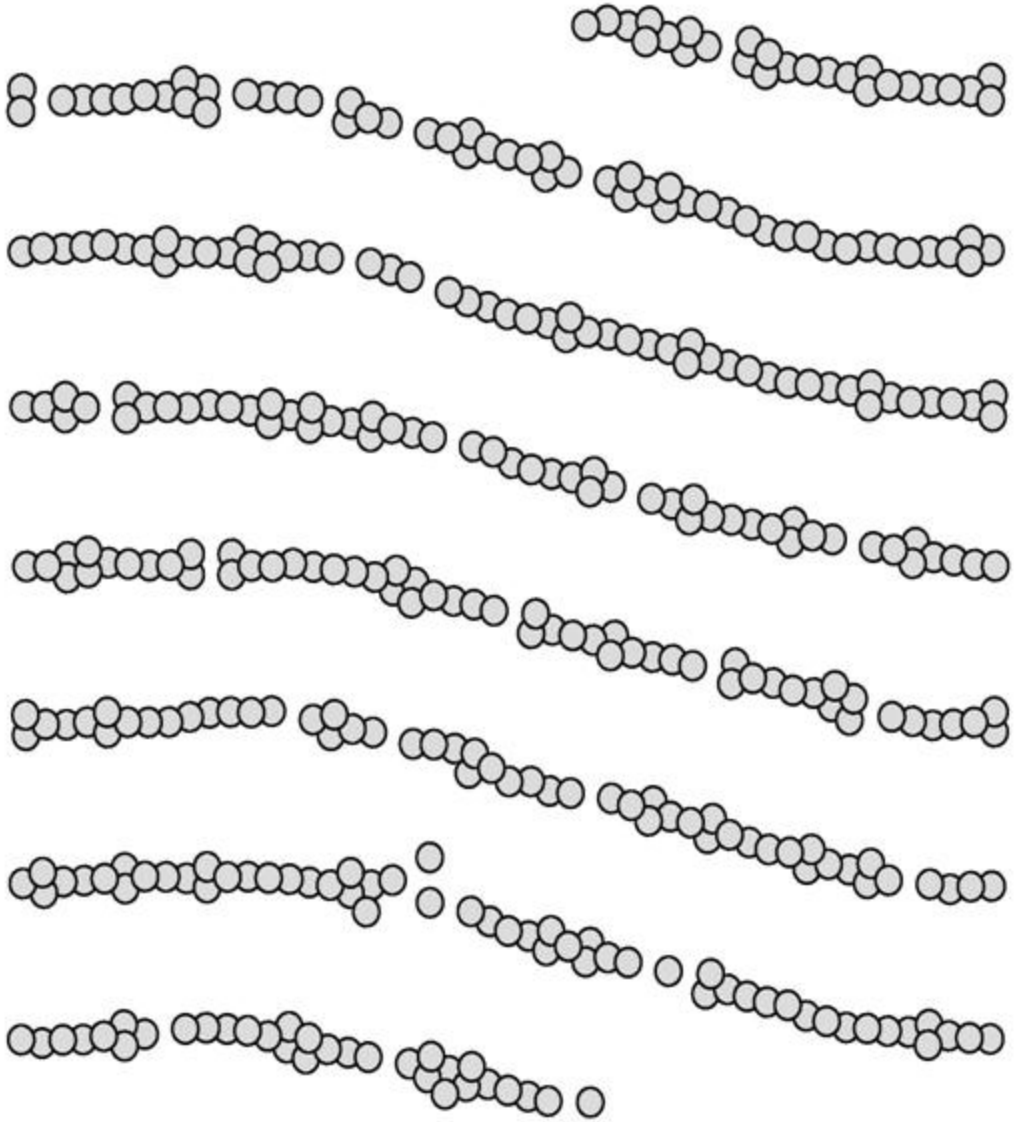
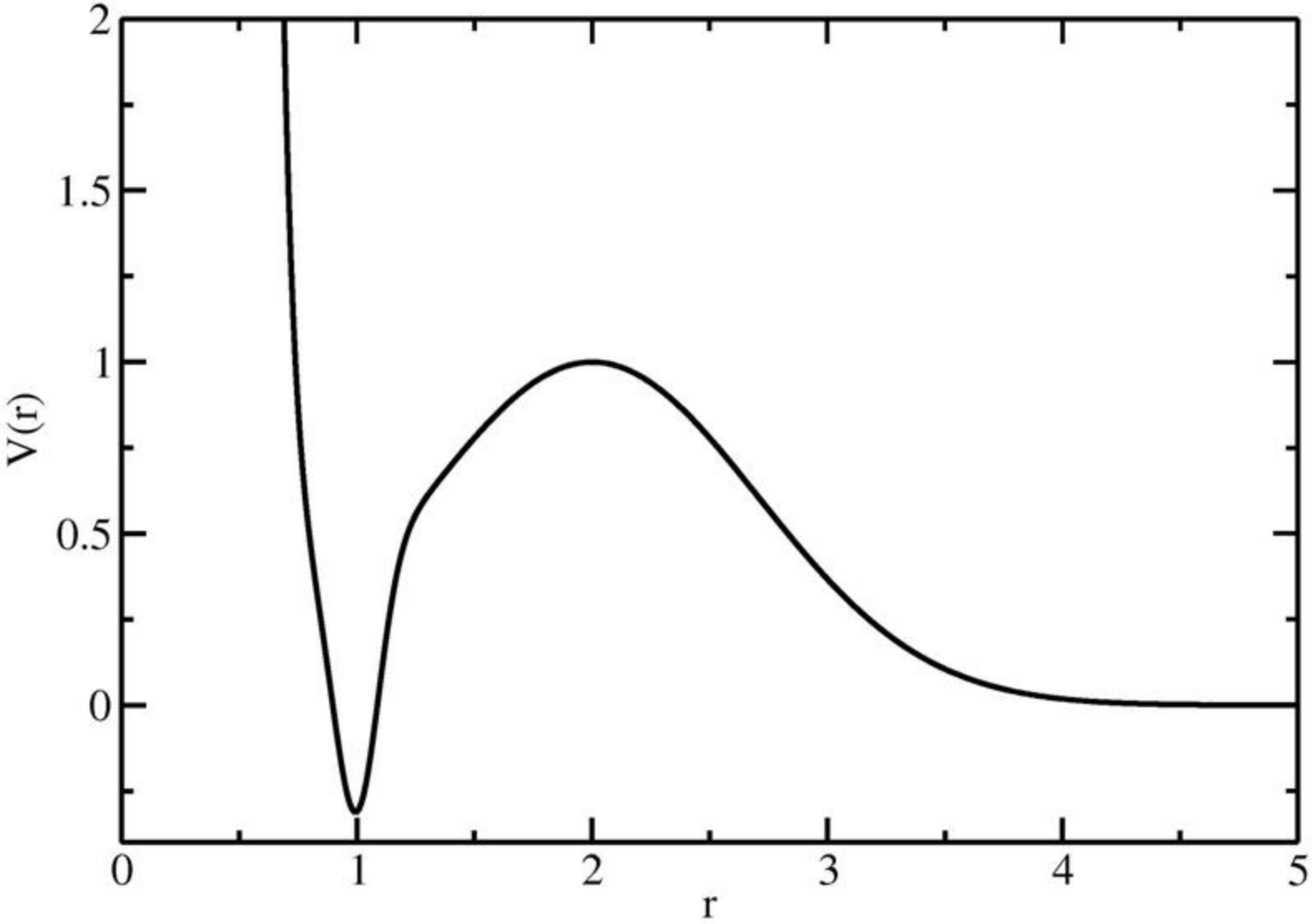
5finger-mc



Simplex potential



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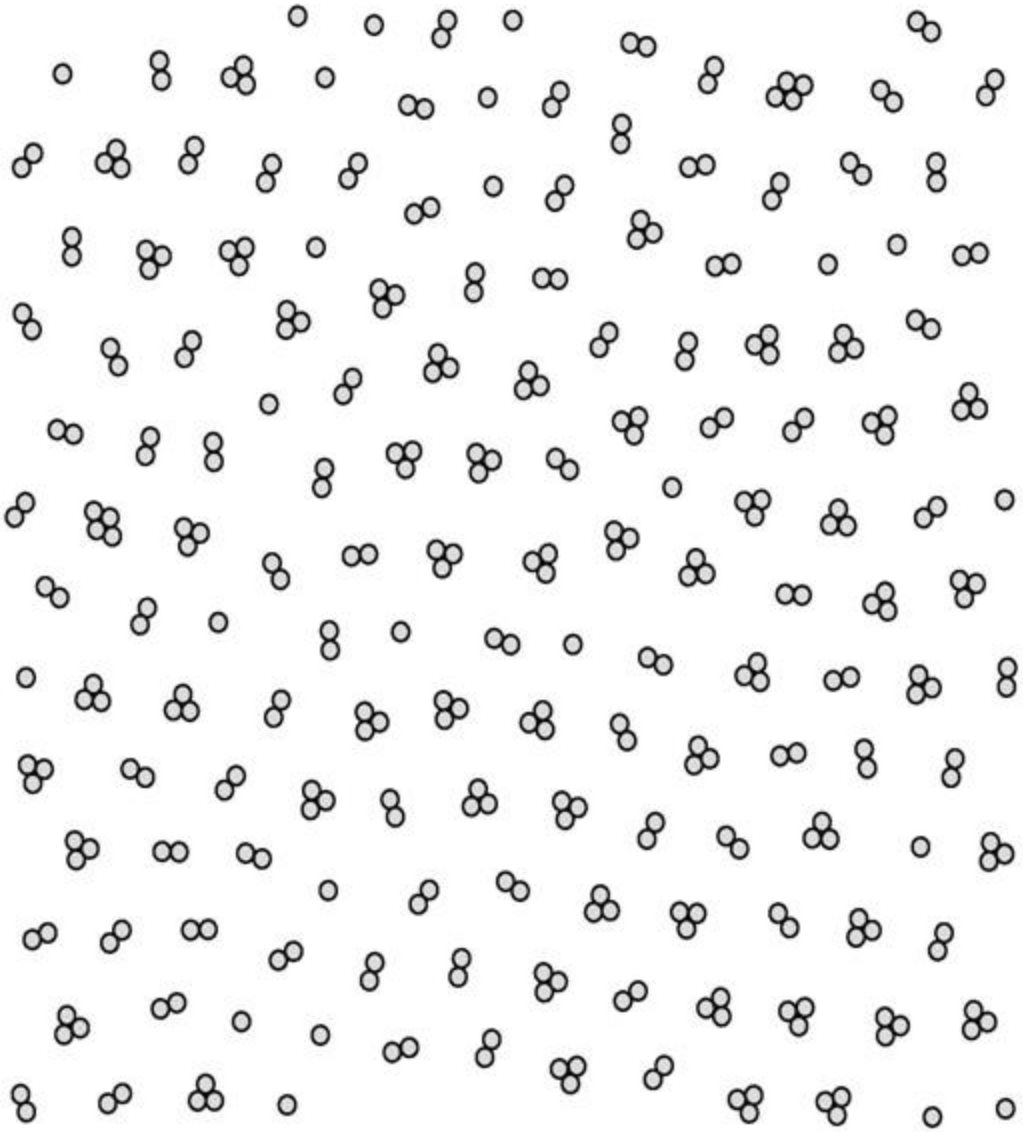
simplex-mc



FINAL COMMENTS

(A) Pair potentials that produce degenerate ground state structures can be constructed. In particular "incommensurate solids" (ideal mixtures of particles and vacancies) are possible.

(B) A procedure should be developed to correct $v_2(r)$ for the unintended presence of three-body interactions (as expected in colloid solutions).

(C) Opportunities for targeted structures using 2 or more particle species remains largely unexplored.

(D) Can quasicrystal structures be attainable targets?

(E) Are nanotube structures attainable targets?