Melting scenarios and unusual crystal structures in two-dimensional core-softened systems

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Recently, there has been growing interest to investigation of behavior of confined fluids, with a special attention to the water. Water plays an important role in many natural processes where it is confined or at contact with substrates, for example, in rocks, in biological cells, at contact with surfaces of proteins, in biological membranes, etc. It is well known, that the qualitative behavior of water, including the water-like anomalies, can be described using the core-softened potentials with two length scales. Another example of the core-softened system which also demonstrates complex phase behavior and water-like anomalies is the Hertzian spheres

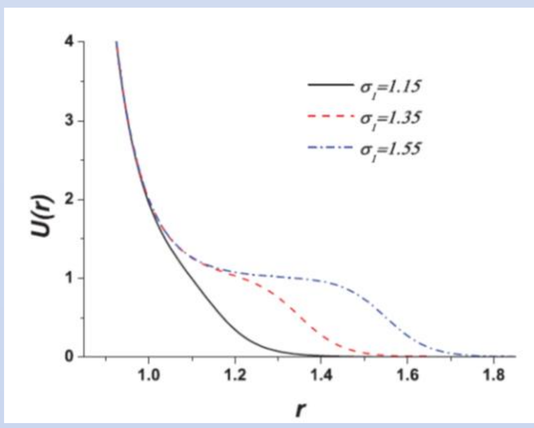
Three melting scenarios

1. Berezinskii-Kosterlitz-Thouless-Halperin-Nelson-Young (BKTHNY) theory – dissociation of bound dislocation and disclination pairs through two BKT transitions with the intermediate hexatic phase [1-5].
2. First-order transition [4-5].
3. Two-stage transition with continuous BKT type solid-hexatic transition and first order hexatic-liquid transition.

Systems

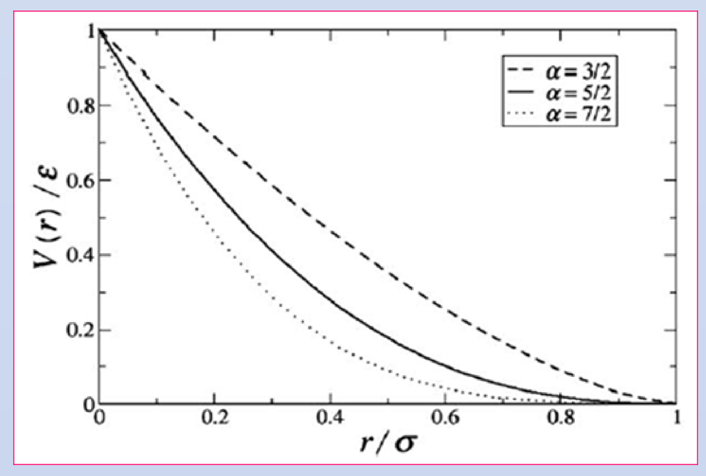
Core-softened potential – water-like anomalies
Yu. D. Fomin, N.V. Gribova, V.N.Ryzhov, S.M. Stishov, and Daan Frenkel, J. Chem. Phys. 129, 064512 (2008));

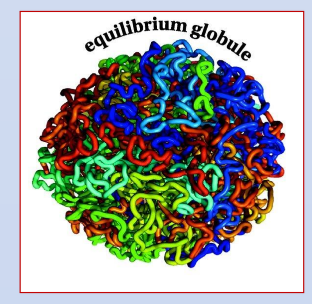
$$U(r) = \varepsilon\left(\frac{\sigma}{r}\right)^{14} + \frac{1}{2}\varepsilon(1 - \tanh(k_0[r - \sigma_1]))$$



The Hertz potential - model for the soft matter systems (polymer globule, etc.)

$$U(r_{ij}) = \frac{\varepsilon}{\alpha}\left(1 - \frac{r_{ij}}{\sigma}\right)^{\alpha}\Theta\left(1 - \frac{r_{ij}}{\sigma}\right)$$



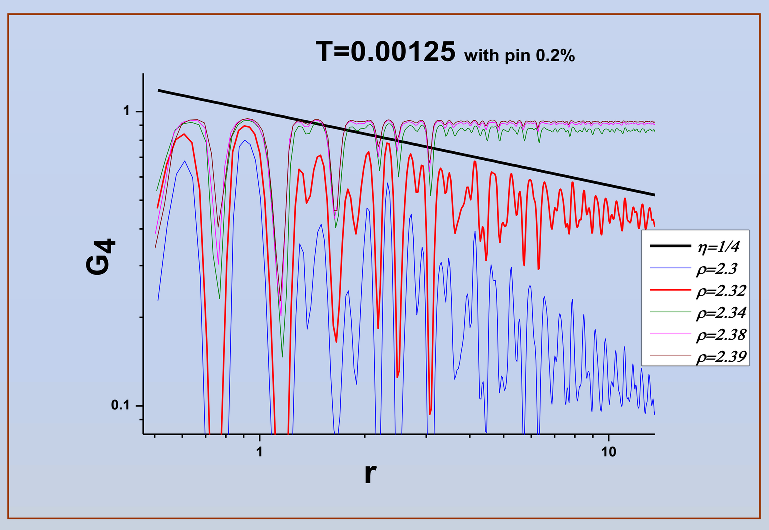


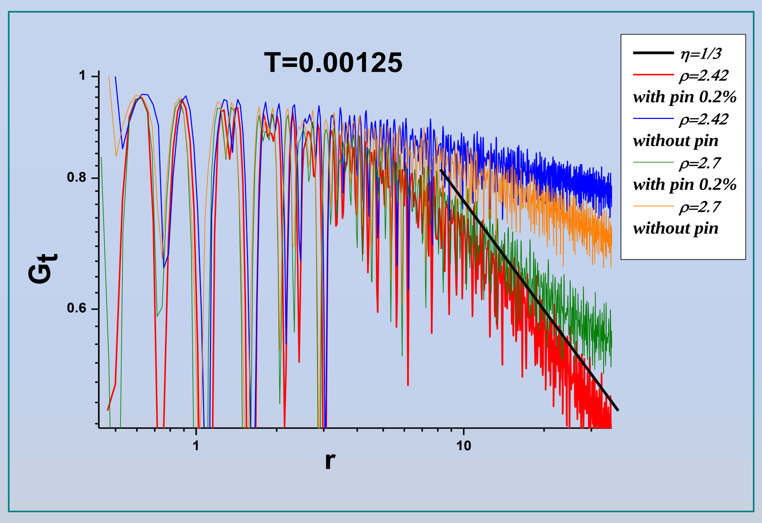
Method

- **Molecular Dynamics Simulation (LAMMPS package).**
- **NVT and NVE ensembles, N = 20 000 (Triangle) and N = 22 500 (Square)**

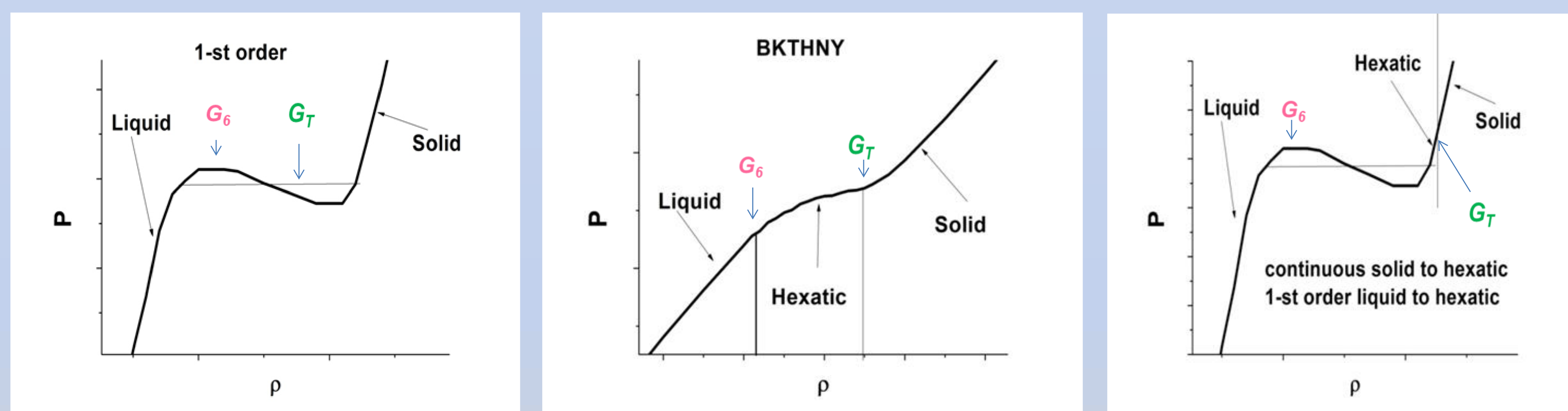
Criteria for determining the melting scenario

1. The behavior of the orientational correlation function (G4,6) and the long-range translational correlation function (Gt)



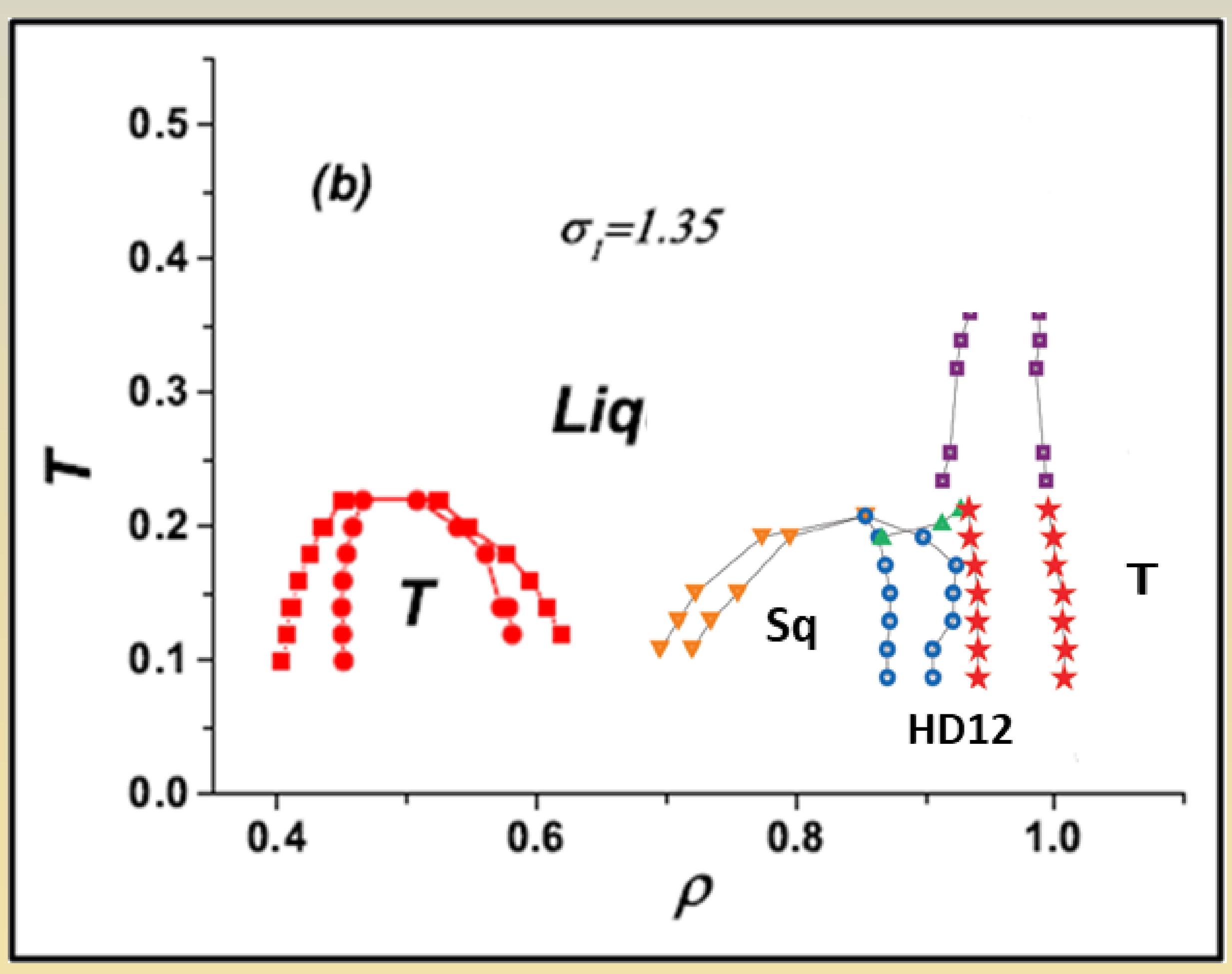


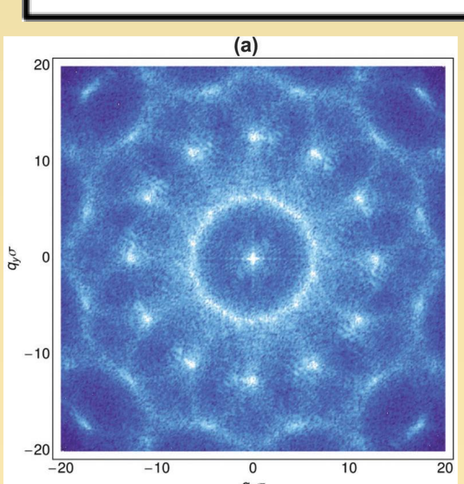
2. Equations of states for three melting scenarios of 2D systems (V.N. Ryzhov, E.E. Tareyeva, Yu.D. Fomin, E.N. Tsiok, Physics Uspekhi 60, 857 (2017)).



First-order transition ***BKTHNY scenario*** ***First-order liquid-hexatic and continuous hexatic-solid transition***

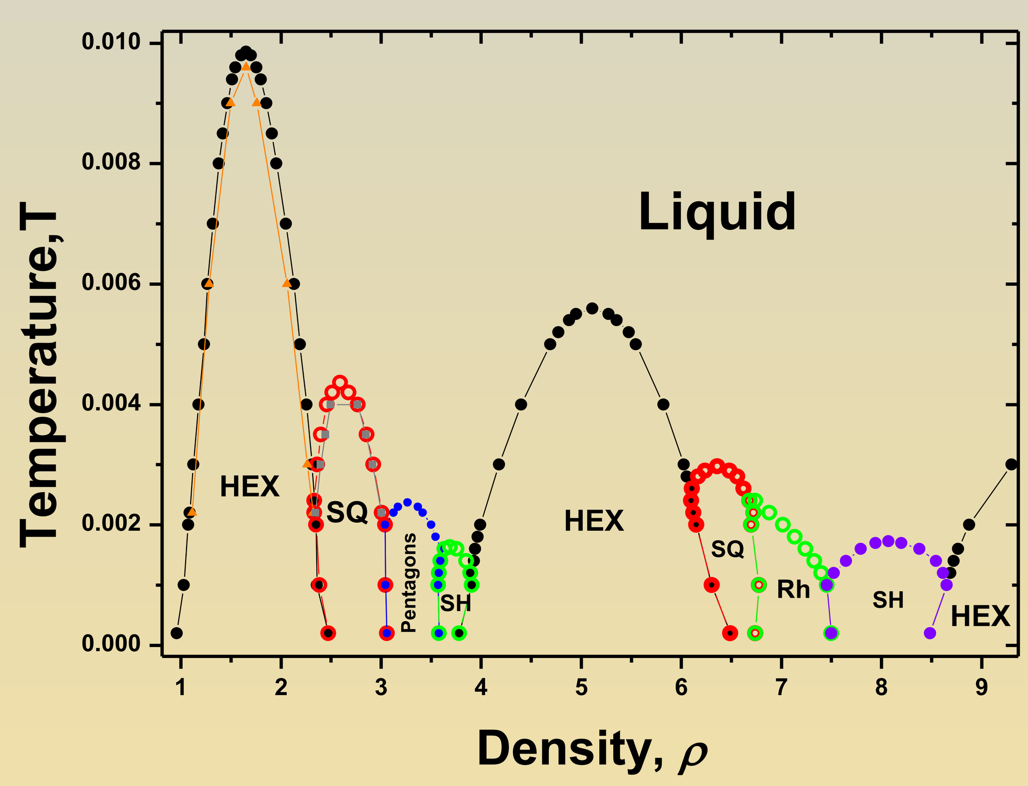
Phase diagram of core-softened system in the (a) r–T and (b) P–T plane, including the areas of liquid, square (sq), hexagonal (hex) crystals, as well as the quasicrystalline phase (HD12).
(N. P. Kryuchkov, S. O. Yurchenko, Y. D. Fomin, E. N. Tsiok and V. N. Ryzhov, Soft Matter 14, 2152 (2018))



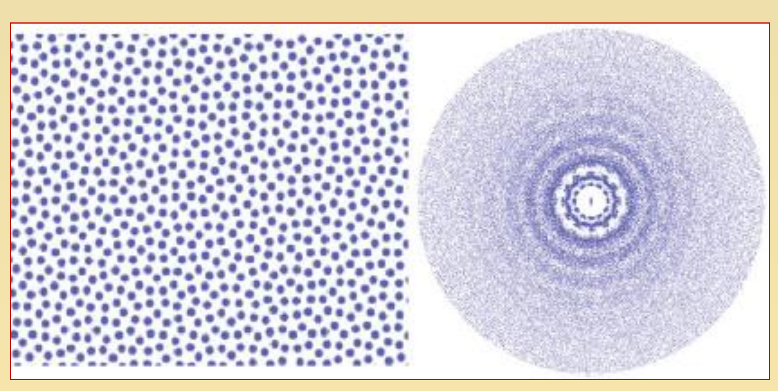


A diffraction pattern of the dodecagonal quasicrystal HD12

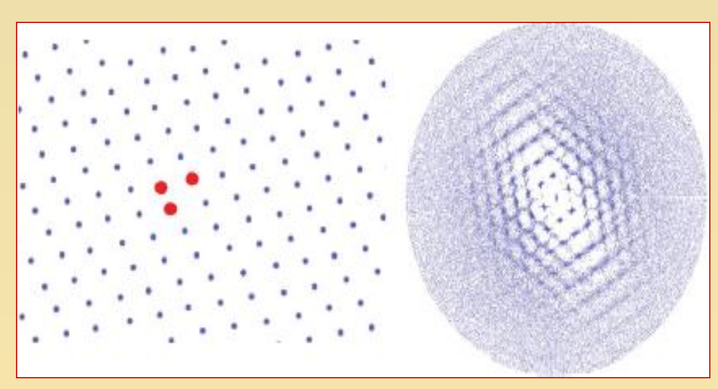
Phase diagram of Hertzian spheres, $\alpha = 5/2$
(Yu. D. Fomin, E. A. Gaiduk, E. N. Tsiok & V. N. Ryzhov, The phase diagram and melting scenarios of two-dimensional Hertzian spheres, Molecular Physics, 116 (21-22), 3258-3270 (2018))



The notation of solid phases is as follows: HEX: triangular crystal; SQ: square crystal; Pentagons: dodecagonal quasicrystal; SH: stretched triangular phase; RH: rhombohedral crystal.



Left panel: an example of a snapshot of the dodecagonal quasicrystal (ρ = 3.4, T =0.001). Right panel: a diffraction pattern



Left panel: an example of a snapshot of the stretched triangular crystal phase (ρ = 3.7, T =0.001). Right panel: a diffraction pattern

We have found a large number of ordered phases, including dodecagonal quasicrystal, and analysed the melting scenarios of low-density triangle and square phases. It is interesting that depending on the position on the phase diagram, the system can melt both through the first-order transition and in accordance with the Berezinskii–Kosterlitz–Thouless–Halperin–Nelson–Young scenario (two continuous transitions with an intermediate hexatic phase) as well as according to recently proposed two-stage melting with the first-order hexatic–isotropic liquid transition and continuous solid–hexatic transition. We have also demonstrated the possibility of a tricritical point on the melting line and have found the line of a water-like density anomaly on the phase diagram.

1.J. M. Kosterlitz, D. J. Thouless, J. Phys. C, 6, 1181 (1973).
2.V.L. Berezinskii, Sov. Phys. JETP 32, 493 (1971).
3. V. L. Berezinskii, Sov. Phys. JETP, 34, 610 (1972).
4. V.N. Ryzhov, E.E. Tareyeva, Yu.D. Fomin, E.N. Tsiok “Berezinskyii—Kosterlitz—Thouless transition and two-dimensional melting” Physics Uspekhi 60 (9), 857-885 (2017)
5. V N Ryzhov, E E Tareyeva, Yu D Fomin, E N Tsiok, Complex phase diagrams of systems with isotropic potentials: results of computer simulations, Physics - Uspekhi 63 (5), 417 - 439 (2020)

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