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

Valentin N. Ryzhov, Yury D. Fomin, Elena E. Tareyeva, Elena N. Tsiok

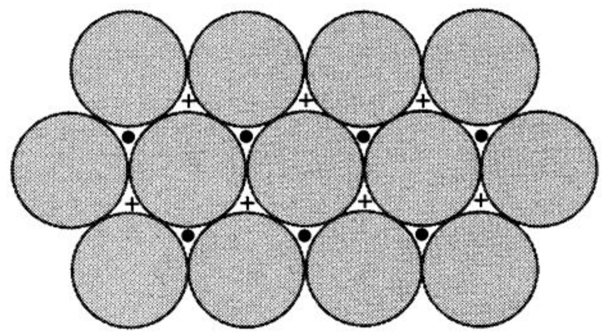
Institute for High Pressure Physics, Russian Academy of Sciences, 108840 Troitsk, Moscow, Russia

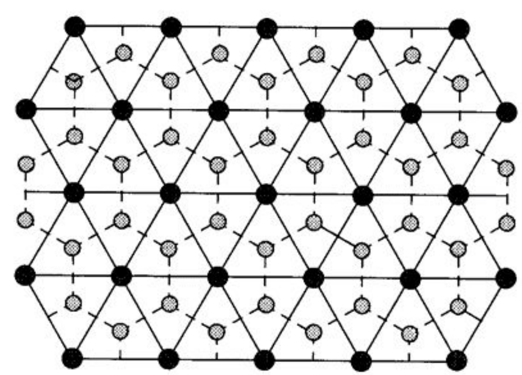
Motivation and Outline

- *Dependence of structural properties and melting scenarios on the shape of the core softened and bound potentials in 2D*
- *Influence of random pinning on the melting scenario of core-softened and bound potential systems*
- *Theoretical background: Berezinskii-Kosterlitz-Thouless transition*
- *Core softened and bound potentials*
- *Theoretical background: Melting scenarios in 2D*
- *Phase diagrams of core-softened and bound potential systems and influence of random pinning on the melting of these systems*

Computer simulations and experimental study of two-dimensional (2D) systems

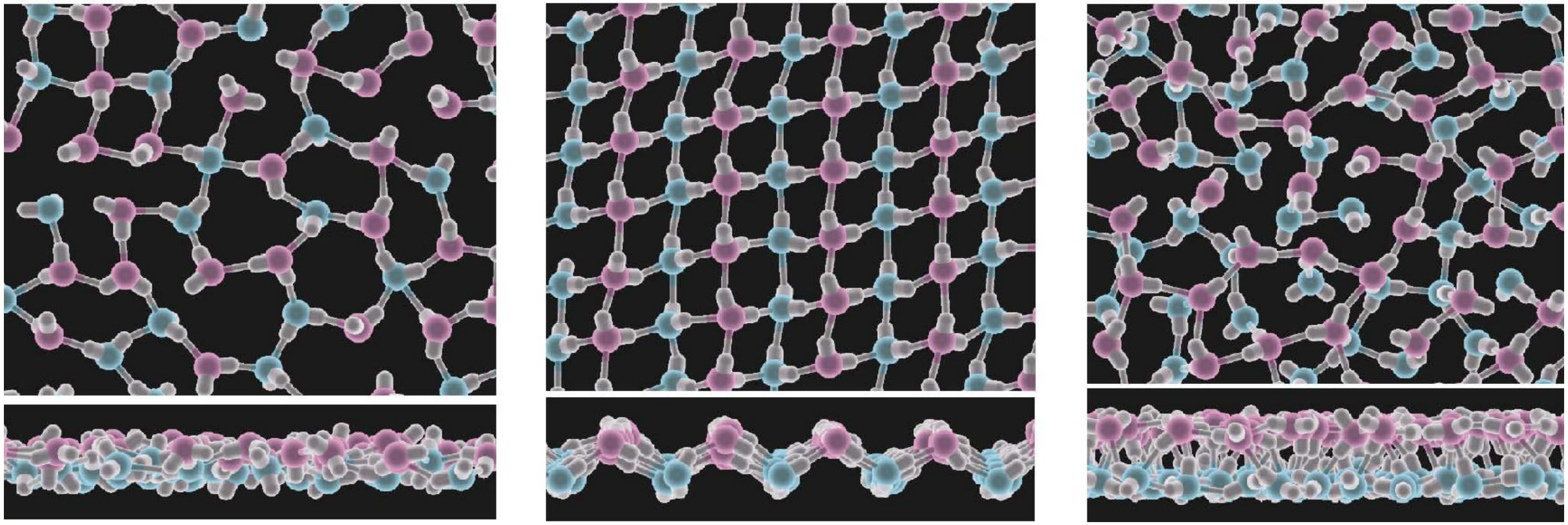
For simple potentials (hard disks, soft disks, Lennard-Jones, etc.) ground state - closed packed triangle crystal structure:





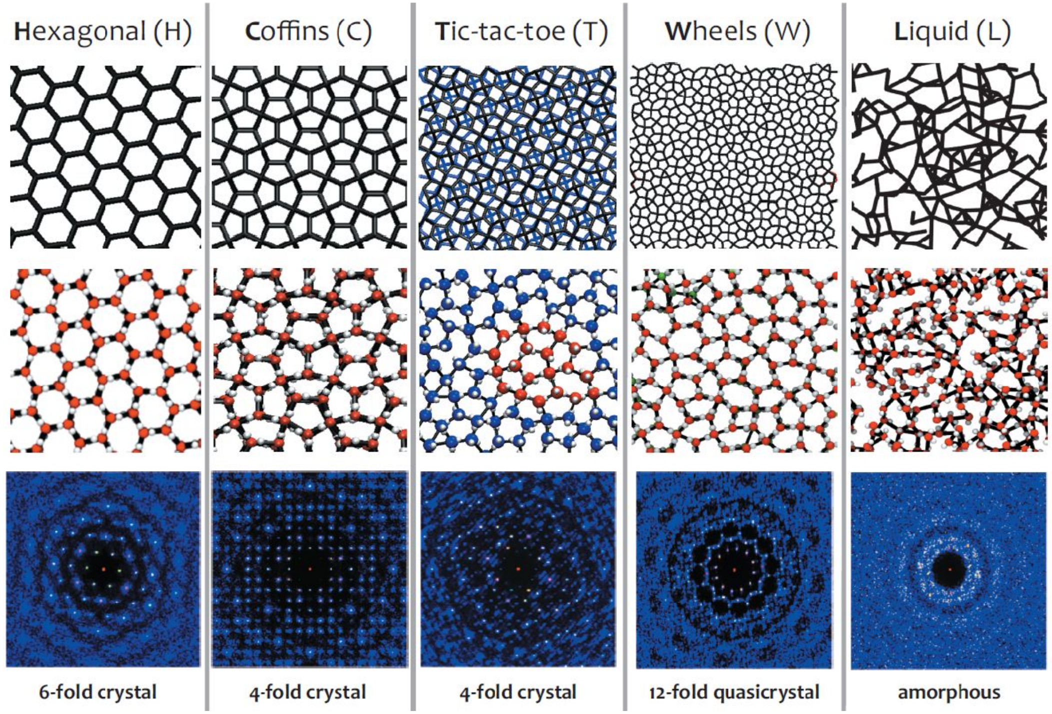
Computer simulations and experimental study of water in slit pores

Monolayer ice: simulation results for the TIP5P model of water in a quasi-two-dimensional hydrophobic slit nanopore (Ronen Zangi* and Alan E. Mark, Phys. Rev. Lett. 91, 025502 (2003); P. Kumar, S. V. Buldyrev, F. W. Starr, N. Giovambattista, and H. Eugene Stanley, Phys. Rev. E 72, 051503 (2005)) . First-order transition into square phase.

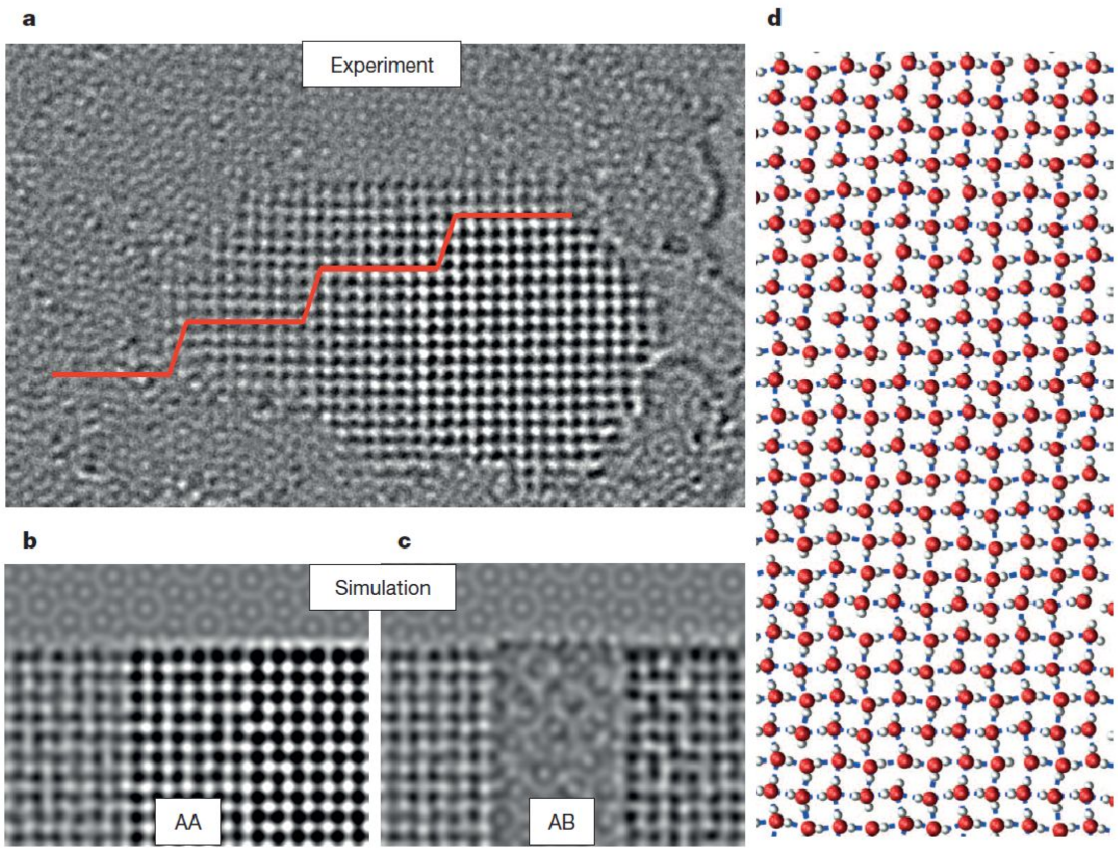


Computer simulations and experimental study of water in slit pores

***The phase diagram of two layers of (TIP4P and mW) water confined between parallel non hydrogen bonding walls** (Jessica C. Johnston, Noah Kastelowitz, and Valeria Molinero, THE JOURNAL OF CHEMICAL PHYSICS 133, 154516 (2010))*

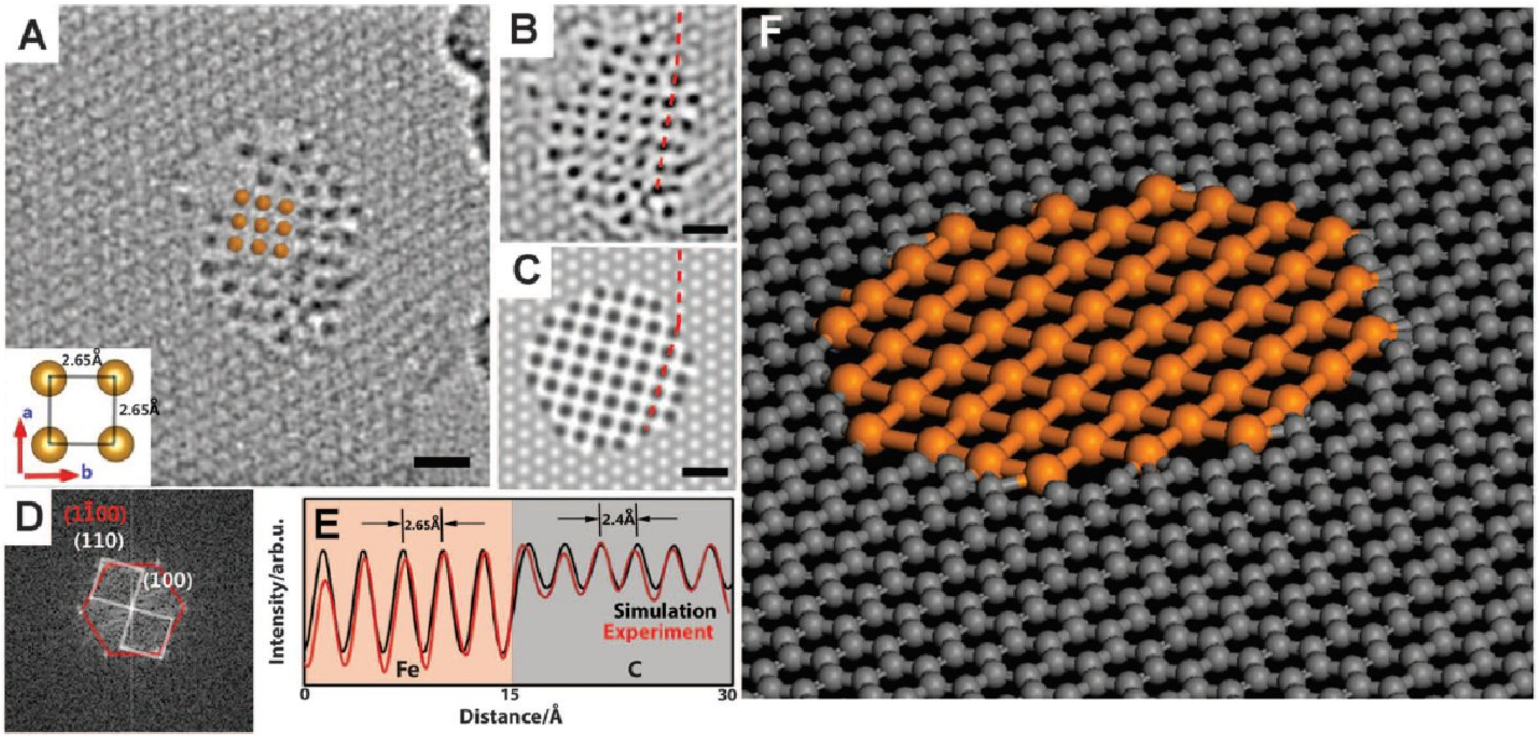


Computer simulations and experimental study of water in slit pores



The nanoconfined between two graphene sheets water at room temperature forms 'square ice'- a phase having symmetry qualitatively different from the conventional tetrahedral geometry of hydrogen bonding between water molecules. Square ice has a high packing density with a lattice constant of 2.83A˚ and can assemble in bilayer and trilayer crystallites ***(G. Algara-Siller, O. Lehtinen, F. C. Wang, R. R. Nair, U. Kaiser, H. A.Wu, A. K. Geim & I. V. Grigorieva, NATURE 5 1 9, 443 (2015)).***

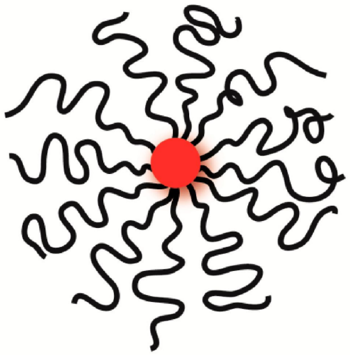
Single-Atom-Thick Iron Membranes Suspended in Graphene Pores (Jiong Zhao et al., Science **343**, 1228 (2014))

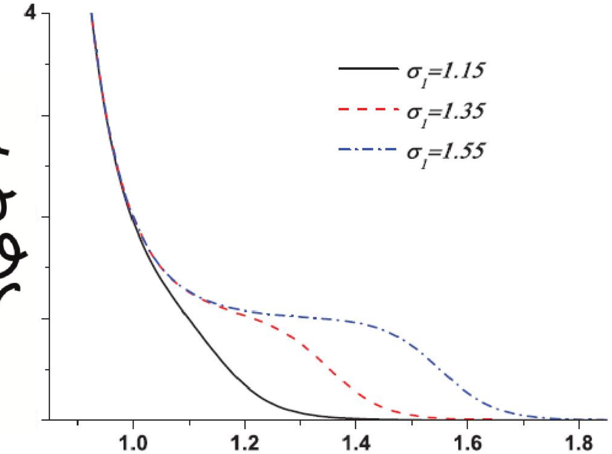


Smooth Repulsive Shoulder Potentials (Yu. D. Fomin, N.V. Gribova, V.N.Ryzhov, S.M. Stishov, and Daan Frenkel, J. Chem. Phys. 129, 064512 (2008)); *Hertzian spheres* (Yu. D. Fomin, E. A. Gaiduk, E. N. Tsiok and V. N. Ryzhov, Molecular Physics, DOI: 10.1080/00268976.2018.1464676 (2018)).

Smooth Repulsive Shoulder System (SRSS)

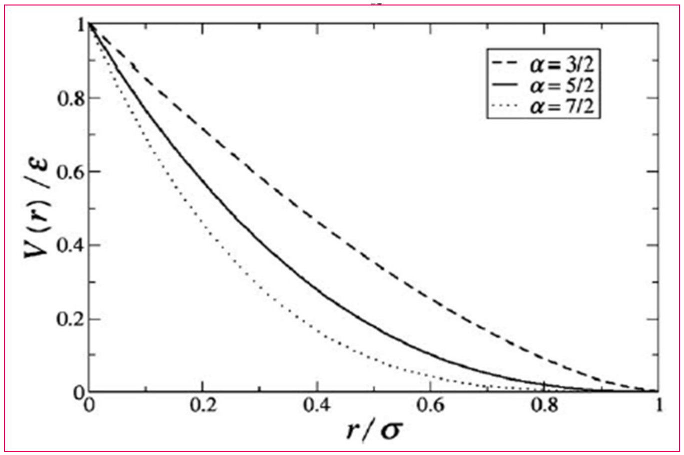
$$U(r) = \varepsilon \left(\frac{\sigma}{r}\right)^{14} + \frac{1}{2}\varepsilon(1 - \tanh(k_0[r - \sigma_1]))$$

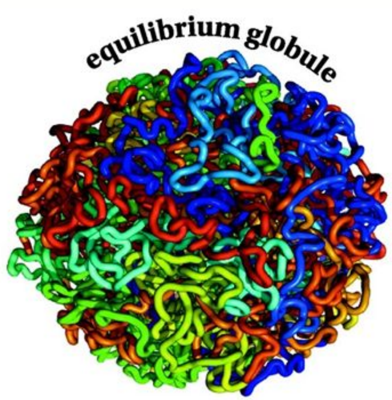




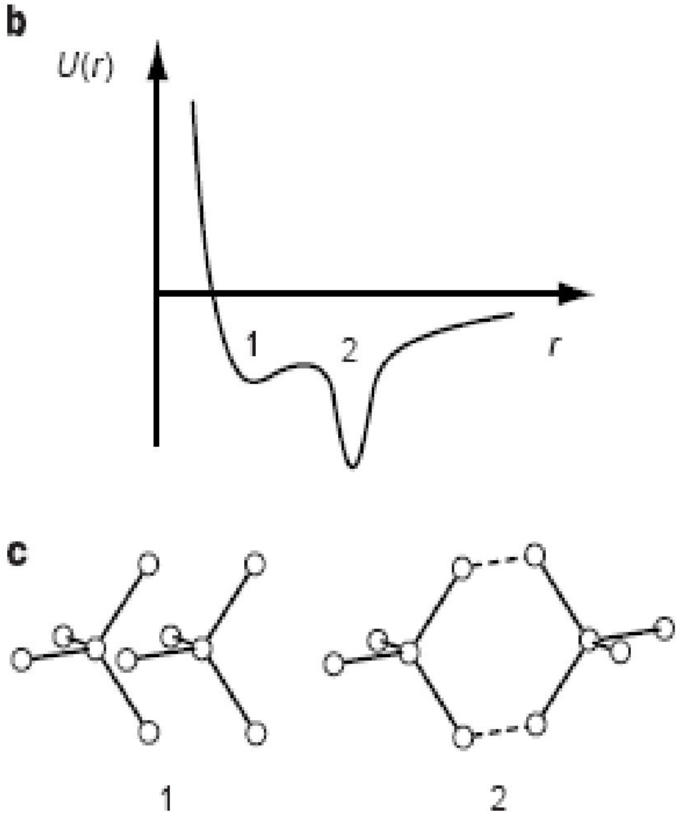
Hertzian spheres system

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





Effective potential for water (O.Mishima and H.E. Stanley, Nature 396, 329 (1998))



Traditional MD computer water models (ST2,SPC,TIP3P,TIP4P,TIP5P) replace 3 nuclei and 18 electrons interacting via quantum mechanics by a few point charges and 3 point masses interacting via classical mechanics

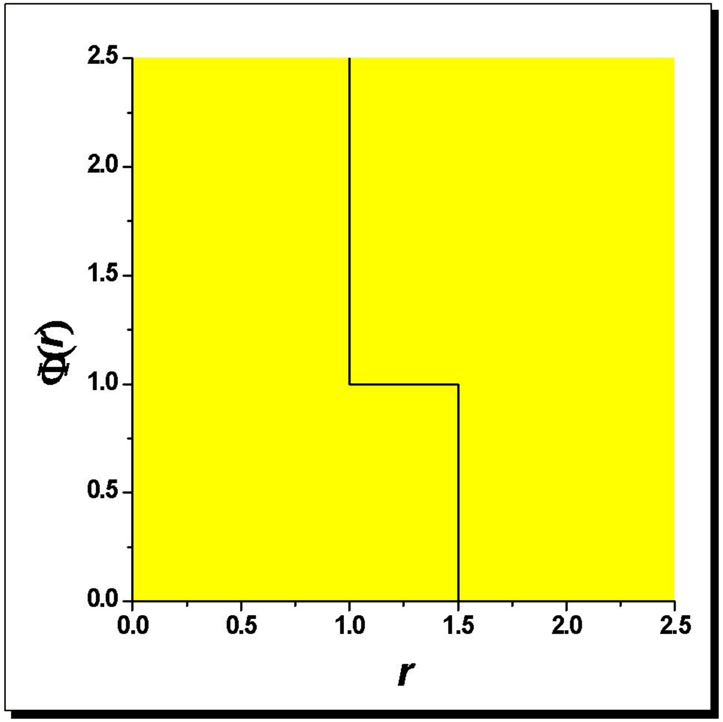
Why not to do further simplifications?

Repulsive-shoulder potential

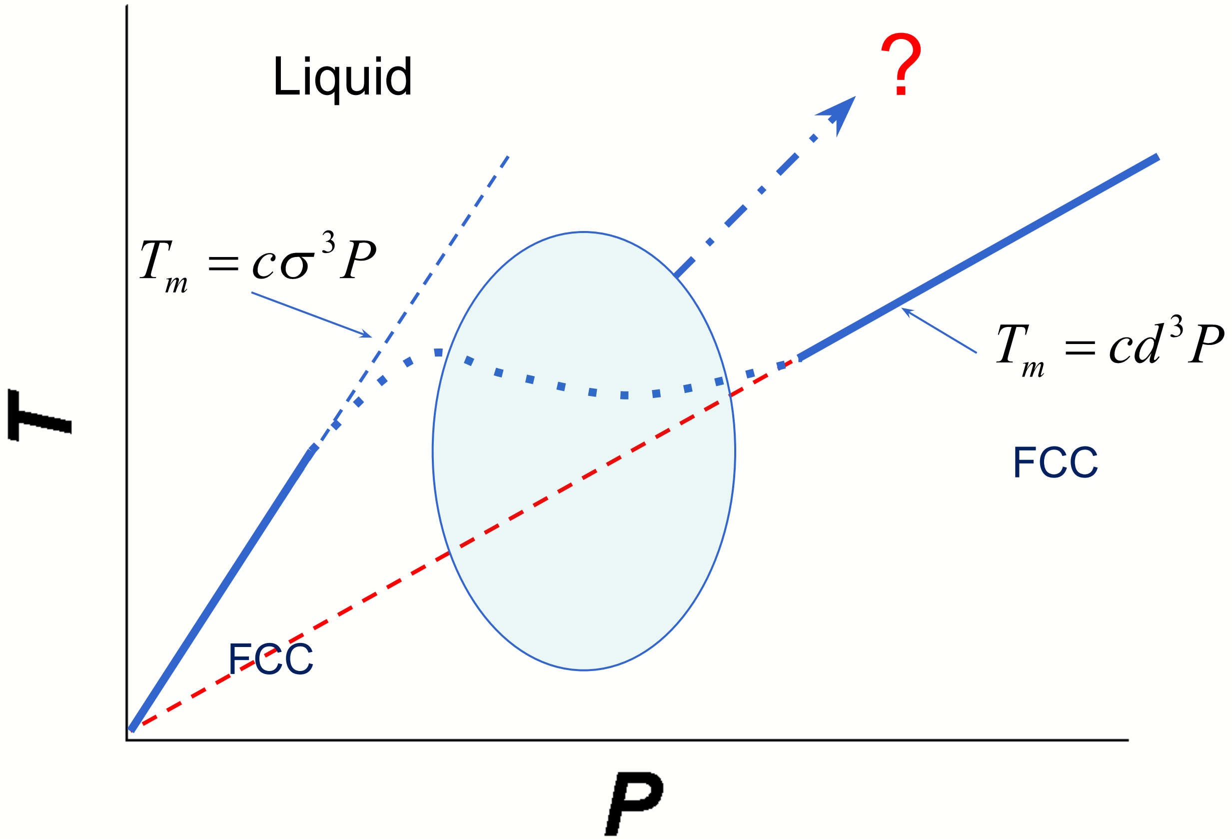
- *D.A.Young and B.J.Alder, Phys. Rev. Lett. **38**, 1233 (1977), S. M. Stishov, Phil. Mag. B **82**, 1287 (2002)*

$$\Phi(r) = \begin{cases} \infty, & r \le d \\ \varepsilon, & d < r \le \sigma \\ 0, & r > \sigma \end{cases}$$

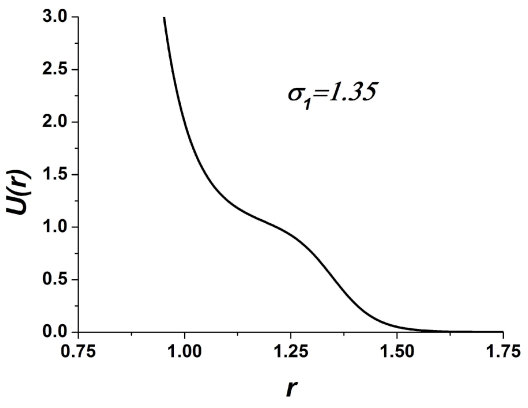
d - diameter of the hard core
***σ** – width of the repulsive step*
ε – height of the repulsive step



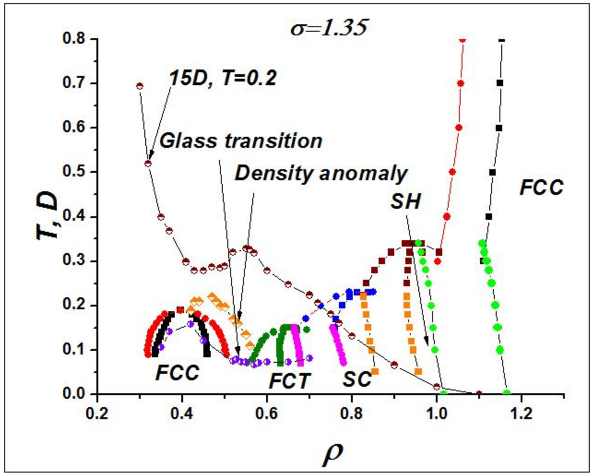
Hypothetical phase diagram of the repulsive-shoulder potential

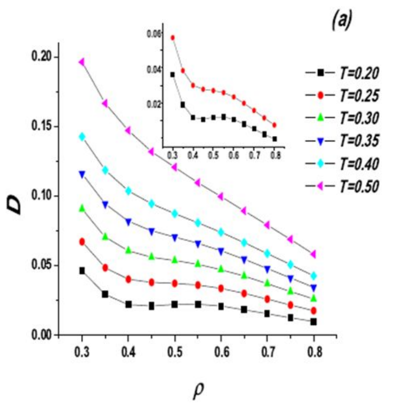


Phase diagrams and anomalies for SRSS (Yu. D. Fomin, N.V. Gribova, V.N.Ryzhov, S.M. Stishov, and Daan Frenkel, J. Chem. Phys. 129, 064512 (2008); Yu.D. Fomin, V.N. Ryzhov, and E.N. Tsiok, J. Chem. Phys. 134, 044523 (2011); Phys. Rev. E 87, 042122 (2013); R.E. Ryltsev, N.M. Chtchelkatchev, and V.N. Ryzhov, Phys. Rev. Lett. 110, 025701 (2013)).

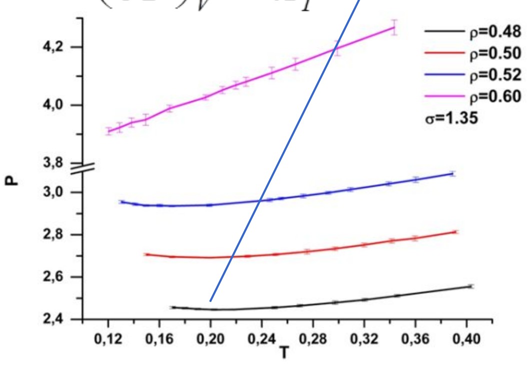


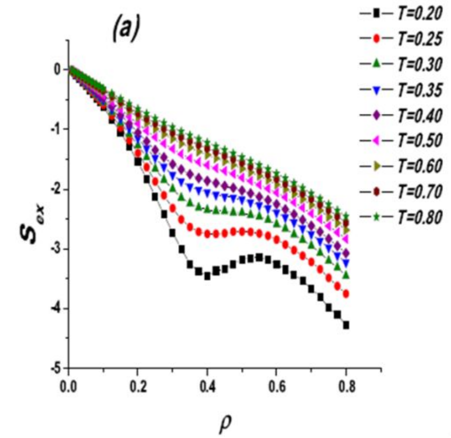
Phase diagram for σ =1.35 (with diffusion and density anomalies and glass transition).





$$\left(\frac{\partial P}{\partial T}\right)_V = \frac{\alpha_P}{\kappa_T} \quad \kappa_T > 0 \quad \alpha_P < 0$$





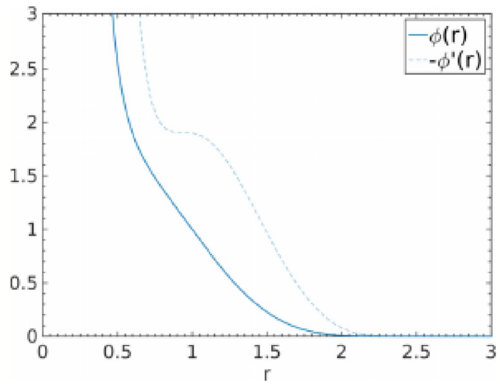
Computer simulations of core softened models – non-triangle structures (some examples)

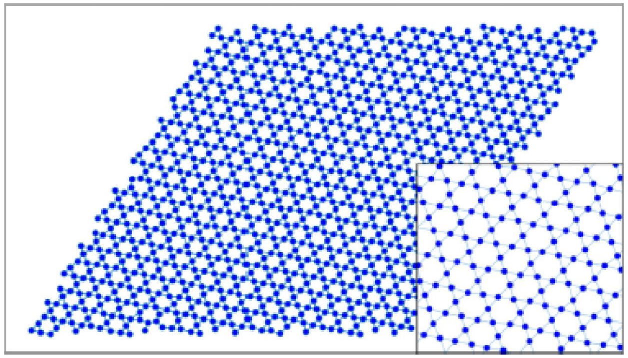
THE JOURNAL OF CHEMICAL PHYSICS 145, 054901 (2016)

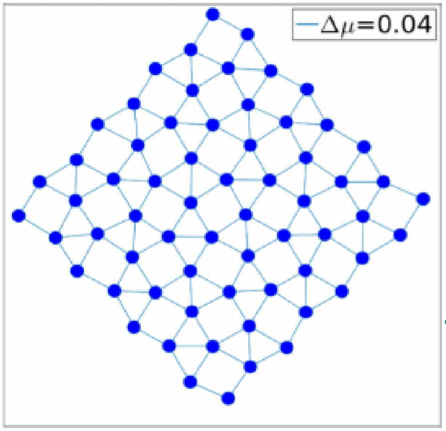
Designing convex repulsive pair potentials that favor assembly of kagome and snub square lattices

William D. Piñeros,[1] Michael Baldea,[2] and Thomas M. Truskett[2]

$$\phi(r/\sigma) = \epsilon\{A(r/\sigma)^{-n} + \sum_{i=1}^{2} \lambda_i(1 - \tanh[k_i(r/\sigma - \delta_i)])$$
$$+ f_{\mathrm{shift}}(r/\sigma)\}H[(r_{\mathrm{cut}} - r)/\sigma],$$



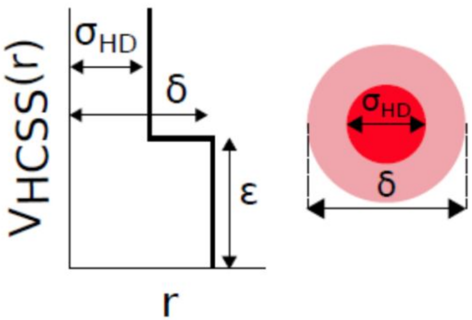


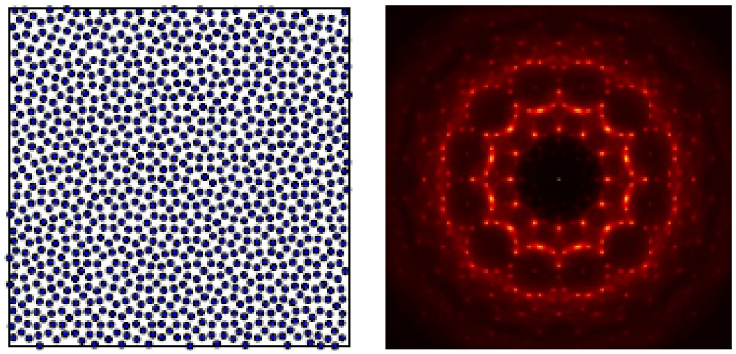


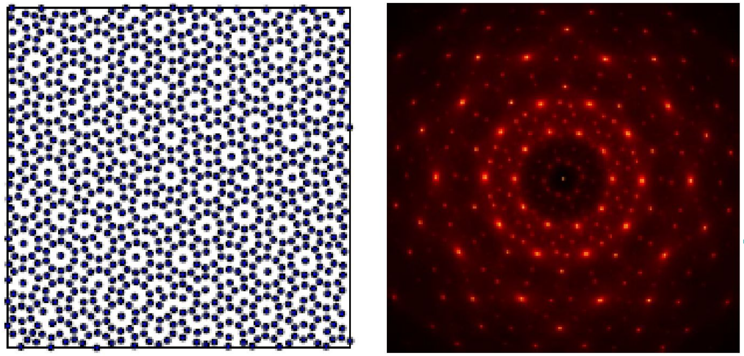
Kagome and equilateral snub square lattices

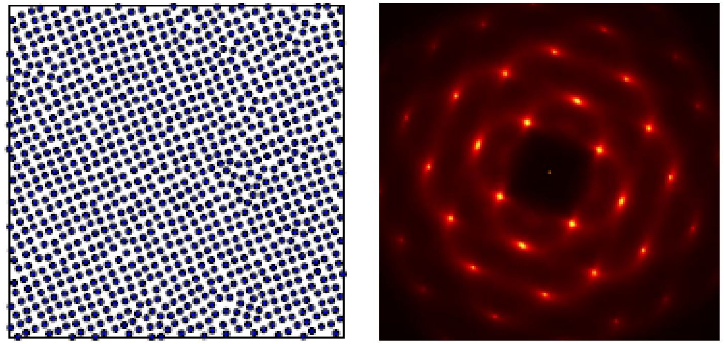
Computer simulations of core softened models – non-triangle structures (some examples)

Quasicrystal structures for hard-core square shoulder (HCSS) pair potential (T. Dotera, T. Oshiro & P. Ziherl, Nature 509, 208 (2014); H. Pattabhiramana and M. Dijkstra, J. Chem. Phys. 146, 114901 (2017); H. Pattabhiramana and M. Dijkstra, Soft Matter DOI: 10.1039/C7SM00254H) and LJG potential {M. Engel, M. Umezaki, Hans-Rainer Trebin, T. Odagaki, Phys. Rev. B 82, 134206 (2010) (octadecagonal, dodecagonal, and decagonal etc. quasicrystals)



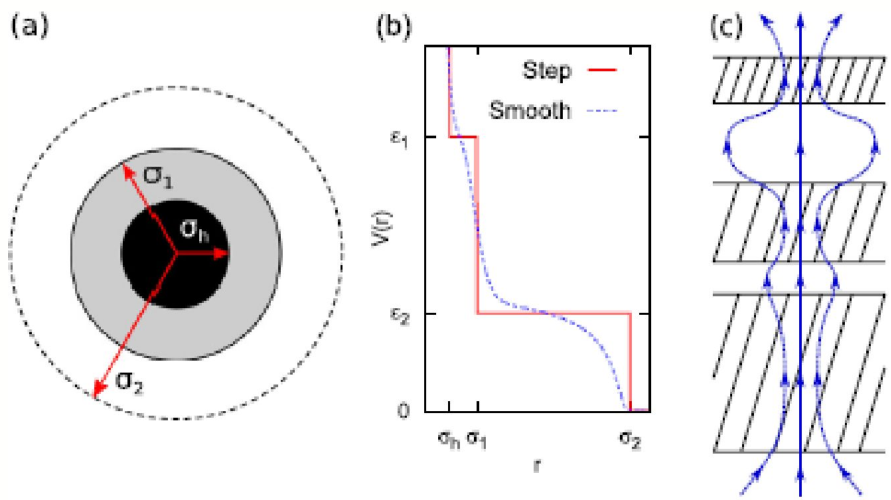


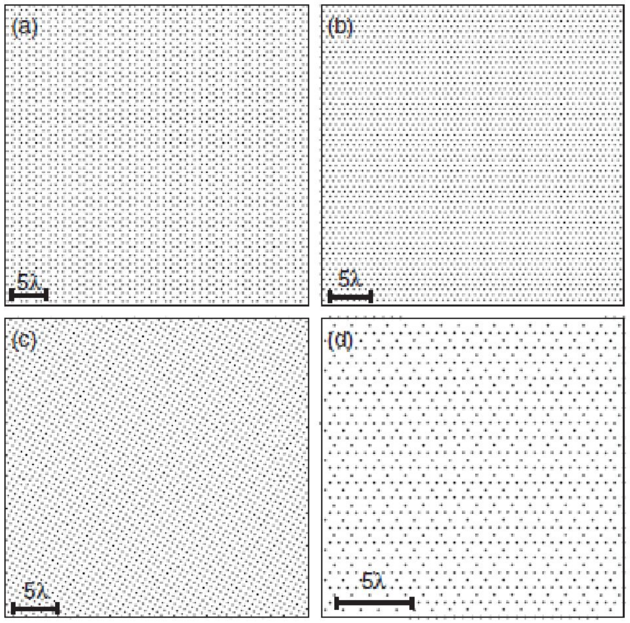




Computer simulations of core softened models – non-triangle structures (some examples)

"Exotic" core softened systems – thin superconducting films (Q. Meng, C. N. Varney, H. Fangohr, and E. Babaev , Phys. Rev. B 90, 020509(R) (2014); J. Phys.: Condens. Matter 29 (2017) 035602; C. N. Varney, K. A. H. Sellin, Qing-Ze Wang, H. Fangohr, and Egor Babaev, J. Phys.: Condens. Matter 25 (2013) 415702)





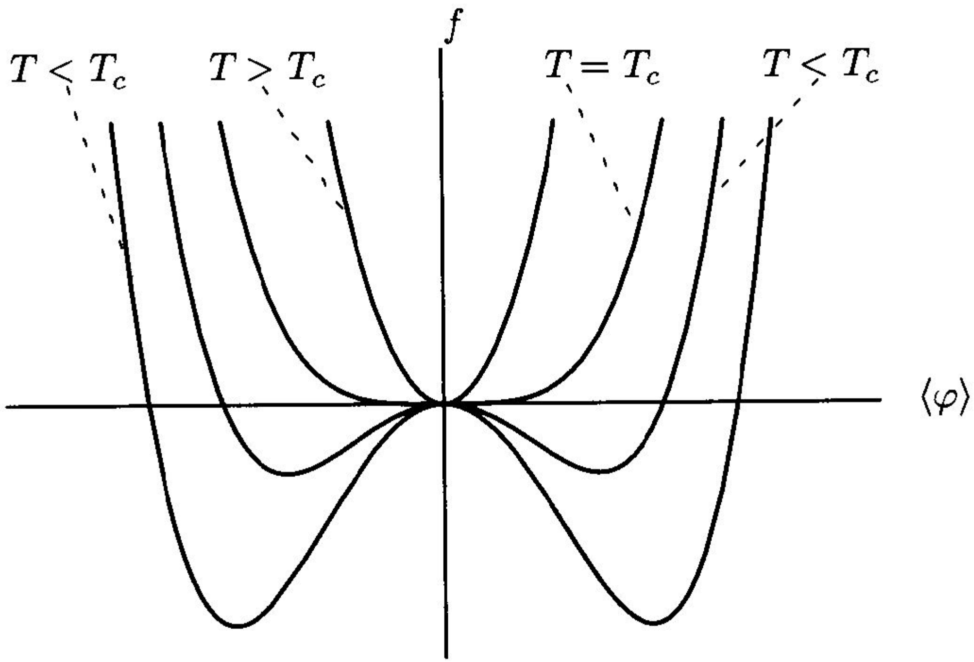
Honeycomb, hexagonal, square and kagome lattices.

Theoretical background: Landau theory of phase transitions - second-order transition (Ising model)

$\langle \phi \rangle$ - Order parameter

$$f(T, \langle \phi \rangle) = \frac{1}{2} r \langle \phi \rangle^2 + u \langle \phi \rangle^4$$

$$r = a(T - T_c).$$



$$\langle \phi \rangle = \begin{cases} 0 & \text{if } T > T_c; \\ \pm(-r/4u)^{1/2} & \text{if } T < T_c. \end{cases}$$

$$\chi = \frac{\partial \langle \phi \rangle}{\partial h} = \begin{cases} 1/r & \text{if } T > T_c; \\ 1/(2|r|) & \text{if } T < T_c. \end{cases}$$

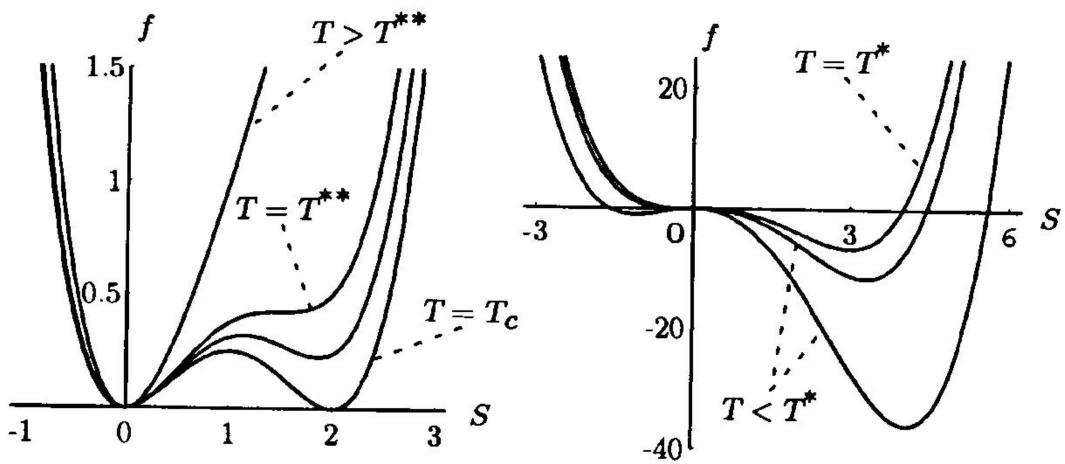
$$c_V = -T \frac{\partial^2 f}{\partial T^2} = \begin{cases} 0 & \text{if } T > T_c; \\ Ta^2/(8u) & T < T_c. \end{cases}$$

Theoretical background: Landau theory of phase transitions - first-order transition (nematic liquid crystal)

Order parameter $$Q_{ij} = \frac{V}{N}\sum_{\alpha}(v_i^{\alpha}v_j^{\alpha} - \frac{1}{3}\delta_{ij})\delta(\mathbf{x} - \mathbf{x}^{\alpha}).$$

$$\langle Q_{ij}\rangle = S(n_i n_j - \frac{1}{3}\delta_{ij}) \qquad S = \frac{1}{2}\langle 3(\mathbf{v}^{\alpha}\cdot\mathbf{n})^2 - 1\rangle = \frac{1}{2}\langle(3\cos^2\theta^{\alpha} - 1)\rangle$$

$$\begin{aligned} f &= \frac{1}{2}r(\frac{3}{2}\mathrm{Tr}\langle \underline{Q}\rangle^2) - w(\frac{9}{2}\mathrm{Tr}\langle \underline{Q}\rangle^3) + u(\frac{3}{2}\mathrm{Tr}\langle \underline{Q}\rangle^2)^2 \\ &= \frac{1}{2}rS^2 - wS^3 + uS^4. \end{aligned} \qquad r = a(T - T^*)$$



Theoretical background: Landau theory of phase transitions - crystallization

Order parameter $$\langle \delta n(\mathbf{x}) \rangle = \langle n(\mathbf{x}) \rangle - n_0 = \sum_{\mathbf{G}} n_{\mathbf{G}} e^{i\mathbf{G}\cdot\mathbf{x}}$$

$$f_{SL} = \frac{F_{SL}}{V} = \sum_{\mathbf{G}} \frac{1}{2} r_{\mathbf{G}} |n_{\mathbf{G}}|^2 - w \sum_{\mathbf{G}_1,\mathbf{G}_2,\mathbf{G}_3} n_{\mathbf{G}_1} n_{\mathbf{G}_2} n_{\mathbf{G}_3} \delta_{\mathbf{G}_1+\mathbf{G}_2+\mathbf{G}_3,0}$$

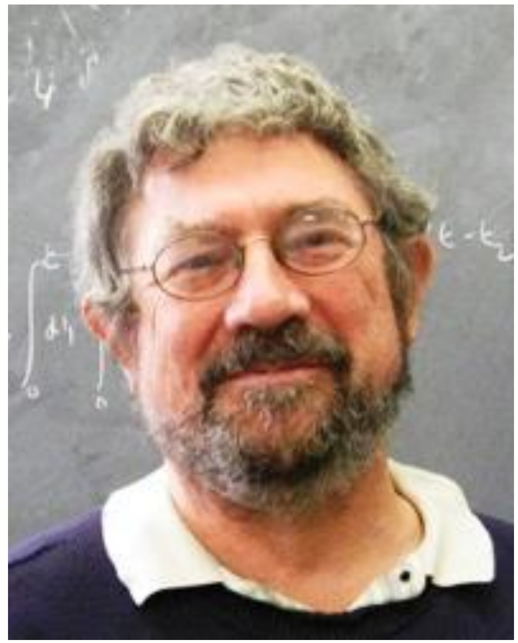
$$+u \sum_{\mathbf{G}_1,\mathbf{G}_2,\mathbf{G}_3,\mathbf{G}_4} n_{\mathbf{G}_1} n_{\mathbf{G}_2} n_{\mathbf{G}_3} n_{\mathbf{G}_4} \delta_{\mathbf{G}_1+\mathbf{G}_2+\mathbf{G}_2+\mathbf{G}_3+\mathbf{G}_4,0},$$

Are all crystals BCC?
(S.Alexander and J.P. McTague, Phys. Rev. Lett. 41, 702 (1978))

Small fluctuations!!!

Theoretical background: Berezinskii-Kosterlitz-Thouless transition (The Nobel Prize in Physics 2016)

ВАДИМ ЛЬВОВИЧ
БЕРЕЗИНСКИЙ
(1935—1980)

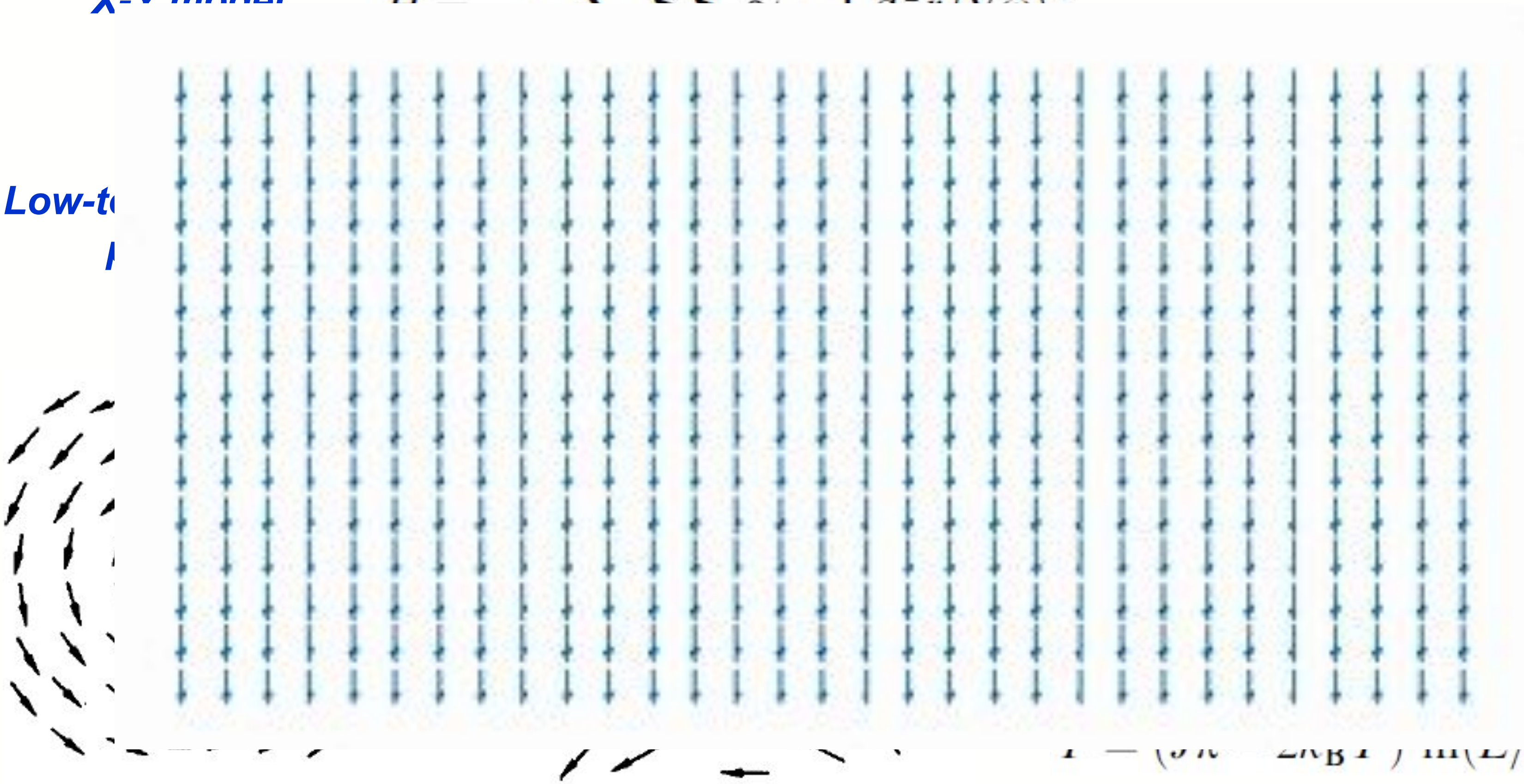


J. Michael Kosterlitz

David Thouless

Theoretical background: Berezinskii-Kosterlitz-Thouless transition (The Nobel Prize in Physics 2016)

X-Y model



Low-t

$\frac{L}{a}$

$\ln(L/a)$ **<0**

Рис. 1. Положительный (а), $q = +1$, и отрицательный (б), $q = -1$, вихри на квадратной решётке.

$$T \geqslant T_{\mathrm{BKT}} = \pi J/(2k_{\mathrm{B}})$$

Theoretical background: Berezinskii-Kosterlitz-Thouless transition and 2D Coulomb Gas

$$\nabla^2 V(r) = -2\pi\delta(\mathbf{r})$$

Poisson's equation

$$V(r) \sim \begin{cases} r, & 1\text{D}, \\ \ln(r), & 2\text{D}, \\ 1/r, & 3\text{D}. \end{cases}$$

Partition function of 2D Coulomb gas

$$Z = \sum_{N-+,N_-=0} \frac{z_+^{N_+}}{N_+!} \frac{z_-^{N_-}}{N_-!} \prod_i \int d^2 r_i \exp\left[-\sum_{i<j} s_i s_j U(r_{ij})/T \right]$$

$$U(r_{ij}) = -\ln(|\mathbf{r}_i - \mathbf{r}_j|)/a \quad z_\pm = \exp(\mu_\pm/T) \quad \mu_\pm = E_c^\pm$$

Theoretical background: Berezinskii-Kosterlitz-Thouless transition and 2D Coulomb Gas

Poisson-Boltzmann equation

$$\nabla^2 U(r) = -2\pi\delta(r) - 2\pi n^+ e^{-U(r)/T} + 2\pi n^- e^{U(r)/T}$$

$$\nabla^2 U(r) = -2\pi\delta(r) - 2\pi n U(r)/T; n = n^+ + n^-$$

$$\hat{U}(k) = \frac{2\pi}{k^2 + \lambda^{-2}}$$

$$\lambda^{-2} = \frac{2\pi n}{T}$$

$$U(r) \propto \begin{cases} \frac{1}{\sqrt{r}} e^{-r/\lambda}, & \lambda \neq \infty \\ -\ln(r), & \lambda = \infty \end{cases}$$

Theoretical background: Berezinskii-Kosterlitz-Thouless transition and 2D Coulomb Gas

$$\left(\frac{a}{\lambda}\right)^2 = g\frac{4\pi z}{T}\left(\frac{a}{\lambda}\right)^{1/2T}$$

$$\left(\frac{a}{\lambda}\right)^2 = \left(g\frac{4\pi z}{T}\right)^{4T/(4T-1)} \quad for \;\; T > \frac{1}{4}$$

$$\lambda^{-2} = 0 \;\; for \;\; T < \frac{1}{4}$$

Infinite order continuous transition

$$F \propto \begin{cases} -\frac{T^2}{2\pi a^2}\left(\frac{4\pi z g}{T}\right)^{4T/(4T-1)}, & T > \frac{1}{4} \\ -\frac{Tz^2}{2\Delta}, & T < \frac{1}{4} \end{cases}$$

Theoretical background: Berezinskii-Kosterlitz-Thouless transition

Two-dimension

$\frac{\mathbf{r}_j|}{} + E_c \sum_i q^2(\mathbf{r}_i)$

Renormalizatic

$\frac{dy(l)}{dl} =$

$\frac{dK^{-1}(l, T}{dl}$

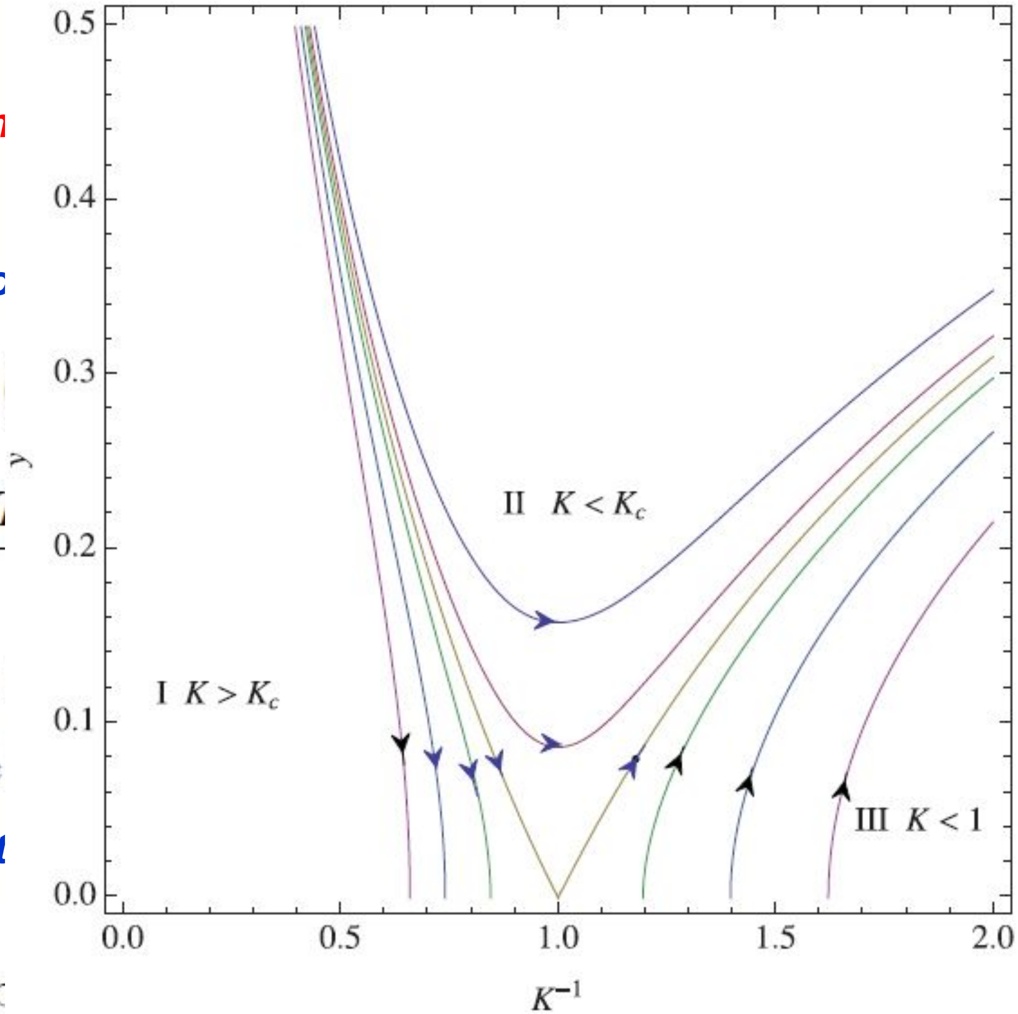
$\frac{\infty, T_{BKT})}{{}_{BKT}} = \frac{2}{\pi}$

где $l = \ln r,$

$y \propto \exp(-E_c$

Correlat

ξ



Theoretical background: Berezinskii-Kosterlitz-Thouless-Halperin-Nelson-Young (BKTHNY) Theory (*M. Kosterlitz and D.J. Thouless, J. Phys. C 6, 1181 (1973); B.I. Halperin and D.R. Nelson, Phys. Rev. Lett. 41, 121 (1978); D.R. Nelson and B.I. Halperin, Phys. Rev. B 19, 2457 (1979); A.P. Young, Phys. Rev. B 19, 1855 (1979)*)

B.I. Halperin

D.R. Nelson

A.P. Young

Berezinskii-Kosterlitz-Thouless-Halperin-Nelson-Young (BKTHNY) Theory

Translational and orientational order in two-dimensional crystals

(N. D. Mermin, Phys. Rev. 176, 250 (1968),
V. N. Ryzhov, E. E. Tareyeva, Yu. D. Fomin, E. N. Tsiok, Phys. Usp. **60**, 857 (2017))

Translational order *Landau L D Phys. Z. Sowjetunion 11 26 (1937); Peierls R E Helv. Phys. Acta 7 81 (1934)*

$$< A >= \frac{\sum_{\mathbf{u}(\mathbf{r})} A e^{-\delta F/k_B T}}{\sum_{\mathbf{u}(\mathbf{r})} e^{-\delta F/k_B T}} \qquad \delta F[\mathbf{u}(\mathbf{r})] = \frac{1}{2}\int \lambda_{ijlm} \frac{\partial u_i}{\partial x_j}\frac{\partial u_l}{\partial u_m} d^2 r$$

$$< u_{i\mathbf{k}} u^*_{l\mathbf{k}} >= \frac{k_B T}{V}\beta^{-1}_{il}(\mathbf{k})$$

где β^{-1}_{ik} - тензор, обратный к β_{il}. Тензор $\beta^{-1}_{il}(k)$ можно записать в виде $[A_{il}(\hat{n})]k^2$, где A_{il} зависит только направления вектора $\mathbf{k} : \hat{n} = \mathbf{k}/k$.

$$< |\mathbf{u}|^2 >= k_B T \int \frac{A_{ii}(\hat{n})}{k^2}\frac{d^2 k}{(2\pi)^2} = \frac{k_B T}{(2\pi)^2}\int_0^{2\pi} A_{ii}(\varphi)\, d\varphi \int_0^{1/d} \frac{dk}{k}$$

$$g_{\mathbf{G}}(|\mathbf{r}_1 - \mathbf{r}_2|) = < \rho(\mathbf{r}_1)\rho(\mathbf{r}_2) > -\bar{\rho}^2 \propto \frac{1}{r^{k_B T \alpha_G}} \cos \mathbf{G}\mathbf{r} \qquad \alpha_G = \frac{G_i G_l A_{il}}{2\pi}$$

Berezinskii-Kosterlitz-Thouless-Halperin-Nelson-Young (BKTHNY) Theory

Orientational order (V. N. Ryzhov, E. E. Tareyeva, Yu. D. Fomin, E. N. Tsiok, Phys. Usp. 60, 857 (2017)

$$\vartheta(x,y) = \frac{1}{2}(\partial_x u_y - \partial_y u_x) \qquad \vartheta(x,y) = \frac{1}{2}\sum_{\mathbf{k}} (ik_x u_{y,\mathbf{k}} - ik_y u_{x,\mathbf{k}})\, e^{i\mathbf{kr}}$$

$$< \vartheta^2 >= \frac{k_B T}{(4\pi)^2} \sum_{ij} \int_0^{2\pi} f_i(\varphi) f_j(\varphi) A_{ij}(\hat{n})\, d\varphi \int_0^{1/d} k\, dk,$$

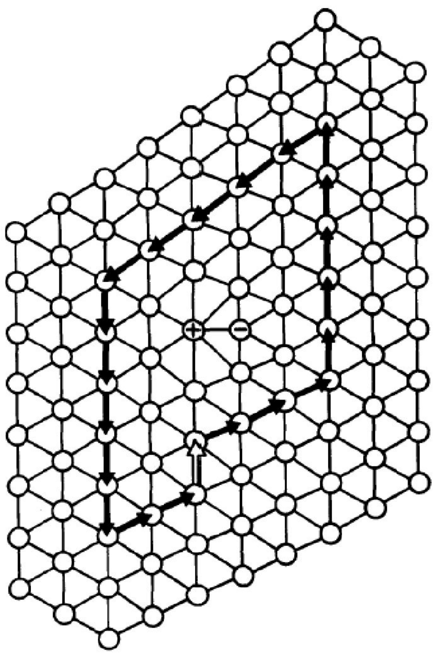
где $f_x(\varphi) = \cos(\varphi)$ и $f_y(\varphi) = \sin(\varphi)$. Таким образом, средний квадрат флуктуаций угла $\vartheta(x,y)$ остается конечным даже для бесконечного образца, т.е. ориентация направления связи "передается"через весь кристалл.

$$< \vartheta(\mathbf{r}_1)\vartheta(\mathbf{r}_2) >= \frac{k_B T}{(4\pi)^2} \sum_{ij} \int_0^{2\pi} f_i(\varphi) f_j(\varphi) A_{ij}(\hat{n})\, d\varphi \int_0^{1/d} \cos \mathbf{k}(\mathbf{r}_1 - \mathbf{r}_2)\, k\, dk$$

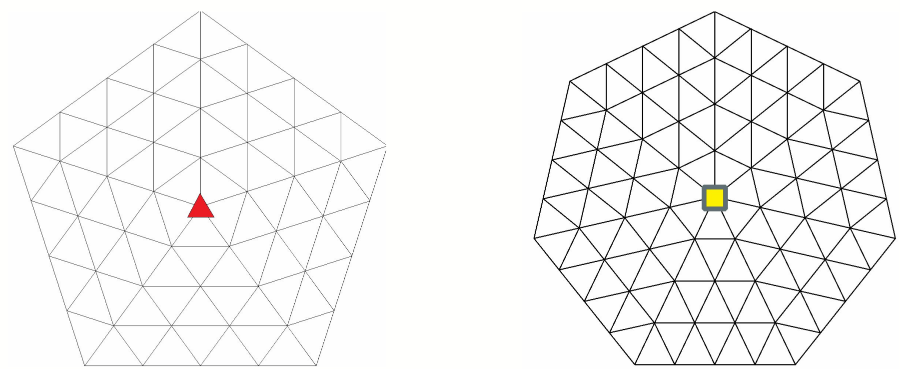
Orientational order is long-ranged!

Theoretical background: BKTHNY theory of 2D melting *(M. Kosterlitz and D.J. Thouless, J. Phys. C 6, 1181 (1973); B.I. Halperin and D.R. Nelson, Phys. Rev. Lett. 41, 121 (1978); D.R. Nelson and B.I. Halperin, Phys. Rev. B 19, 2457 (1979); A.P. Young, Phys. Rev. B 19, 1855 (1979))*

Translational and orientational order: Dislocations and disclinations – main topological defects



Dislocation is a disclination dipole!



Theoretical background: BKTHNY theory – instability of solid phase

Dislocation Hamiltonian

$$H_{dis} = -\frac{a_0^2 K}{8\pi} \sum_{i\neq j}^{M} \left\{ \mathbf{b}(\mathbf{r}_i)\mathbf{b}(\mathbf{r}_j) \ln \frac{r_{ij}}{a} - \frac{(\mathbf{b}(\mathbf{r}_i)\mathbf{r}_{ij})(\mathbf{b}(\mathbf{r}_i)\mathbf{r}_{ij})}{r_{ij}^2} \right\} +$$

$$+ E_d \sum_{i=1}^{M} \mathbf{b}^2(\mathbf{r}_i),$$ where E_d - dislocation core energy.

$$K = \frac{4\mu(\mu+\lambda)}{2\mu+\lambda}$$

Melting is a dissociation of bound dislocation pairs!

At the transition point $g_{\mathbf{G}}(r) \propto r^{-\eta_G}$ $\quad 1/4 \leq \eta_G(T_m) \leq 1/3$

Above transition point $\frac{a_0^2 K}{k_B T} \simeq 16\pi/(1-c|t|^{\nu})$ где $t = (T - T_m)/T_m$, $\nu = 0.3696$

$g_{\mathbf{G}}(r) \propto e^{-r/\xi_+(T)}$ $\quad \xi_+(T) \propto \exp(c/|t|^{\nu})$

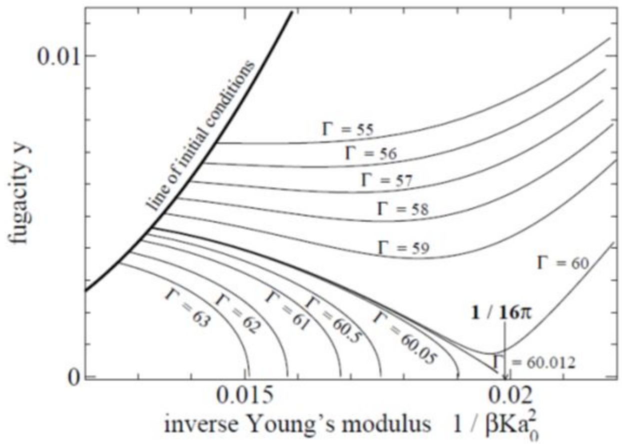
Theoretical background: BKTHNY theory – instability of solid phase

Renormalization group equations

$$\frac{dK^{-1}(l)}{dl} = \frac{3}{2}\pi y^2 e^{K(l)/8\pi} I_0\Big(K(l)/8\pi\Big) - \frac{3}{4}\pi y^2 e^{K(l)/8\pi} I_1\Big(K(l)/8\pi\Big)$$

$$\frac{dy(l)}{dl} = \Big(2 - \frac{K}{8\pi}\Big) y(l) + 2\pi y^2 e^{K(l)/16\pi} I_0\Big(K(l)/8\pi\Big)$$

$$y = e^{-E_c/k_B T}$$



RG equations exist only for triangle lattice!!!

Theoretical background: BKTHNY theory – hexatic phase

Hexatic phase – quasi-long-range orientational order!

Orientational order parameter

$$\psi(\mathbf{r}) = e^{6i\vartheta(\mathbf{r})}$$

Hamiltonian

$$H_A = \frac{1}{2}K_A(T)\int d^2r\,(\nabla\vartheta(\mathbf{r}))^2 \quad H_{disc} = -\frac{\pi K_A(T)}{36}\sum_{\mathbf{r}\neq\mathbf{r}'} s(\mathbf{r})s(\mathbf{r}')\ln\frac{|\mathbf{r}-\mathbf{r}'|}{a} + E_{cd}\sum_{\mathbf{r}} s^2(\mathbf{r})$$

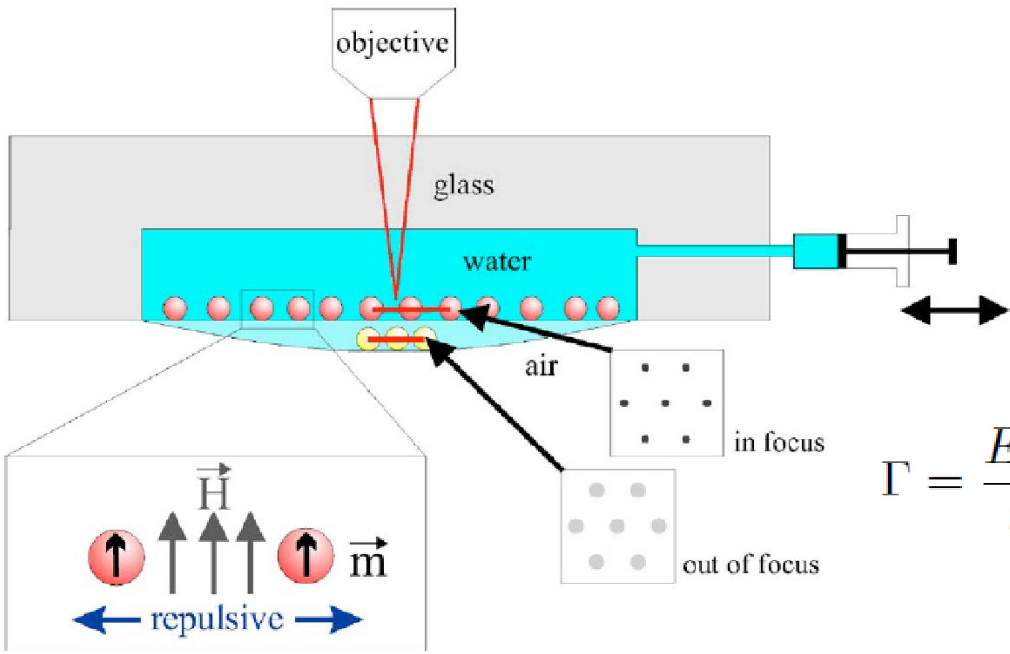
$$T_i = \frac{\pi K_A(T_i)}{72k_B T_i} \qquad <\psi^*(\mathbf{r})\psi(0)>\propto r^{-\eta_6(T)}$$

Continuous BKT transition – dissociation of bound disclination pairs

$$\boxed{\eta_6(T_i) = 1/4}$$

BKTHNY theory – experiment: paramagnetic colloids

(G.Maret et al, Phys. Rev. Lett. 82, 2721 (1999); Phys. Rev. Lett. 85, 3656 (2000); Phys. Rev. Lett. 79, 175 (1997); Phys. Rev. Lett. 92, 215504 (2004); Phys. Rev. E 75, 031402 (2007); Phys. Rev. Lett. 113, 127801 (2014); Phys. Rev. E 88, 062305 (2013); Phys. Rev. Lett. 111, 098301 (2013))

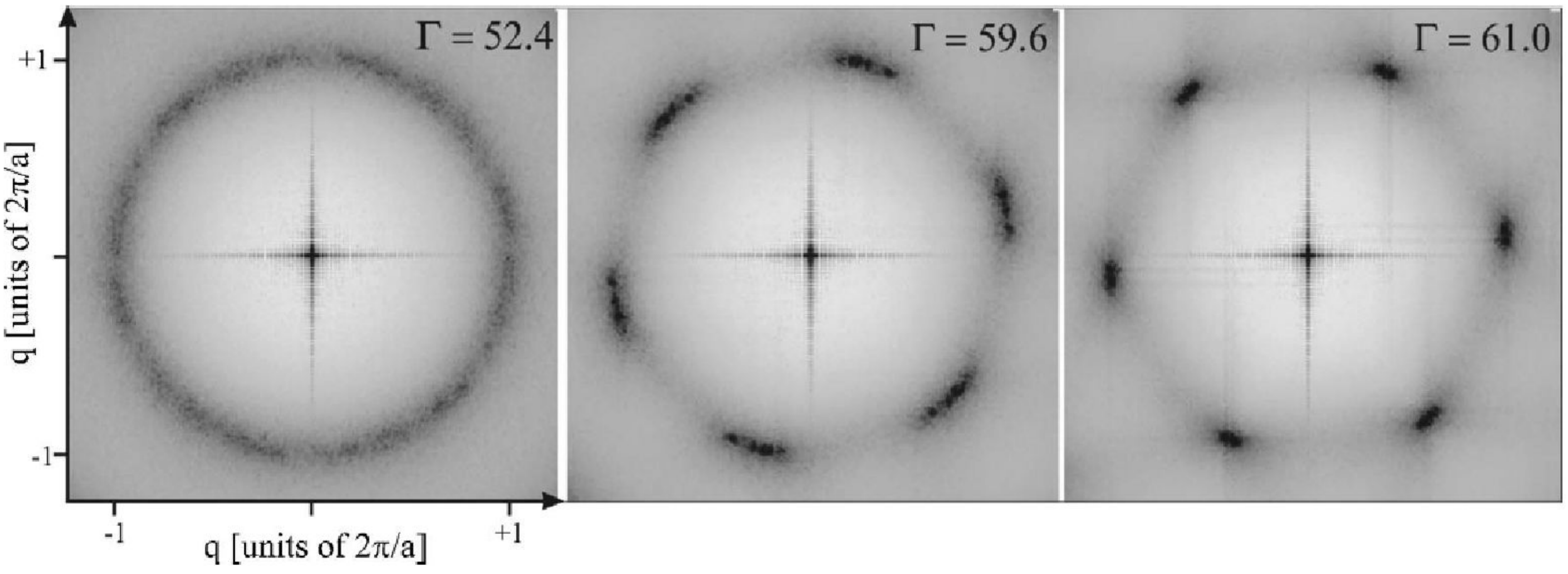


$$\beta v(r) = \frac{\Gamma}{(r/d_{nn})^3}$$

$$\Gamma = \frac{E_{magn}}{k_B T} = \frac{\mu_0}{4\pi} \cdot \frac{\chi^2 \vec{H}^2 \cdot (\pi\rho)^{3/2}}{k_B T} \propto \frac{1}{T_{sys}}$$

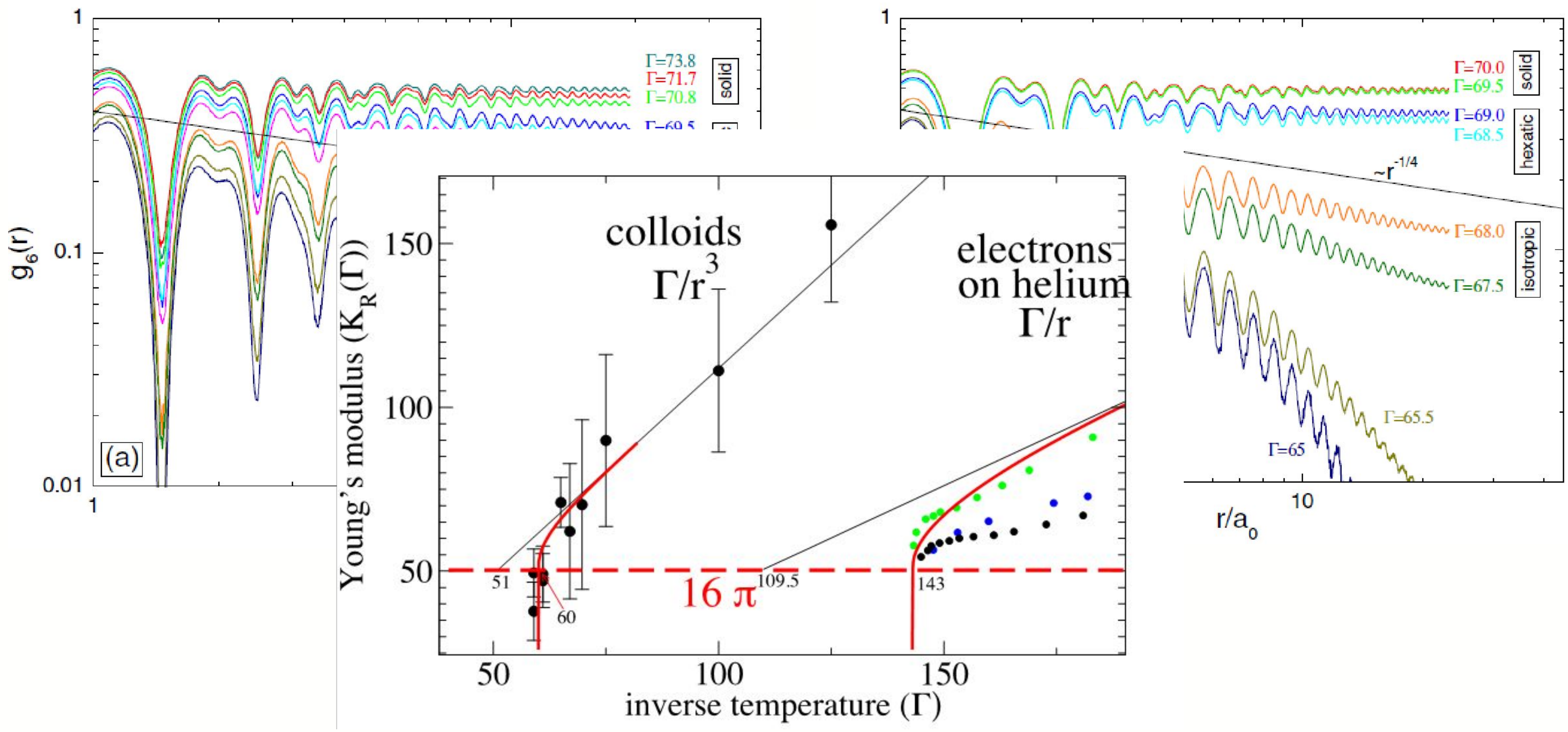
BKTHNY theory – experiment: paramagnetic colloids

Structure factor $S(\vec{q})$



BKTHNY theory – experiment: paramagnetic colloids

Correlation functions and Young modulus

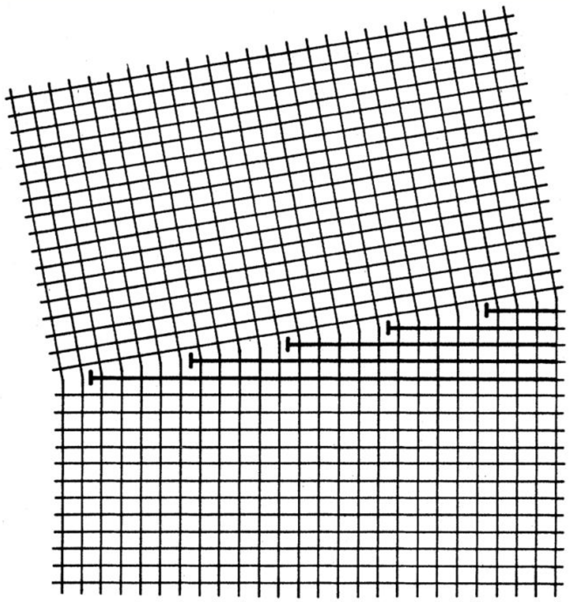


Is BKTHNY theory universal?

Melting scenarios of two-dimensional melting – first-order transition

Proliferation of grain boundaries

(S.T. Chui, Phys. Rev. Lett. 48, 933 (1982); Phys. Rev. B 28, 178 (1983))



$$E_c/k_BT \quad \leq \quad 2.84$$

Dissociation of disclination quadrupoles

V.N. Ryzhov, Dislocation-disclination melting of two-dimensional lattices, Zh. Tksp. Theor. Phys. 100, 1627 – 1639 (1991)

Melting scenarios in two-dimensions: Landau and BKTHNY theories

Order parameter $\rho(\mathbf{r}) = \sum_{\mathbf{G}} \rho_{\mathbf{G}}(\mathbf{r}) e^{i\mathbf{G}\mathbf{r}}$

$$F = \frac{1}{2} a_T \sum_{\mathbf{G}} |\rho_{\mathbf{G}}|^2 + b_T \sum_{\mathbf{G}_1+\mathbf{G}_2+\mathbf{G}_3=0} \rho_{\mathbf{G}_1}\rho_{\mathbf{G}_2}\rho_{\mathbf{G}_3} + O(\rho^4)$$

Landau expansion – first-order transition!

Fluctuations!

The Fourier coefficients vary slowly and have the amplitude and phase

$$\rho_{\mathbf{G}}(\mathbf{r}) = \rho_{\mathbf{G}} e^{i\mathbf{G}\mathbf{u}(\mathbf{r})}$$

*where **u(r)** has the meaning of the displacement field in the crystal. In two dimensions, the phase of the order parameter fluctuates most strongly*

Melting scenarios in two-dimensions: Landau and BKTHNY theories

The Landau expansion of the free energy with the long-wavelength fluctuations of the order parameters:

$$F = \frac{1}{2}\int \sum_{\mathbf{G}} \left[A|\mathbf{G}\times\nabla\rho_{\mathbf{G}}|^2 + B|\mathbf{G}\cdot\nabla\rho_{\mathbf{G}}|^2 + C|\rho_{\mathbf{G}}(\mathbf{G}\cdot\nabla)\rho_{\mathbf{G}}|\right] d^2r +$$

$$+ \frac{1}{2}a_T \sum_{\mathbf{G}} |\rho_{\mathbf{G}}|^2 + b_T \sum_{\mathbf{G}_1+\mathbf{G}_2+\mathbf{G}_3=0} \rho_{\mathbf{G}_1}\rho_{\mathbf{G}_2}\rho_{\mathbf{G}_3} + O(\rho^4).$$

V. N. Ryzhov and E. E. Tareyeva, Phys. Rev. B 51, 8789 (1995); Physica A 314, 396-404 (2002); Physica A 432, 279–286 (2015).

The first term in expansion is the free energy of a deformed solid

$$H_E = \frac{1}{2}\int d^2r\ \left[2\mu u_{ij}^2 + \lambda u_{kk}^2\right], \qquad u_{ij} = \frac{1}{2}\left[\frac{\partial u_i(\mathbf{r})}{\partial r_j} + \frac{\partial u_j(\mathbf{r})}{\partial r_i}\right]$$

The singular part of the displacement field corresponds to dislocations and disclinations

Melting scenarios in two-dimensions: Landau and BKTHNY theories

$$F = \frac{1}{2}\int \sum_{\mathbf{G}} \left[A|\mathbf{G}\times\nabla\rho_{\mathbf{G}}|^2 + B|\mathbf{G}\cdot\nabla\rho_{\mathbf{G}}|^2 + C|\rho_{\mathbf{G}}(\mathbf{G}\cdot\nabla)\rho_{\mathbf{G}}|\right] d^2r +$$

$$+\frac{1}{2}a_T\sum_{\mathbf{G}}|\rho_{\mathbf{G}}|^2 + b_T\sum_{\mathbf{G}_1+\mathbf{G}_2+\mathbf{G}_3=0}\rho_{\mathbf{G}_1}\rho_{\mathbf{G}_2}\rho_{\mathbf{G}_3} + O(\rho^4).$$

Dislocation unbinding temperature T_m.
The modulus of the order parameter vanishes at temperature T_{MF} if the free energies of the liquid and solid phases are equal.

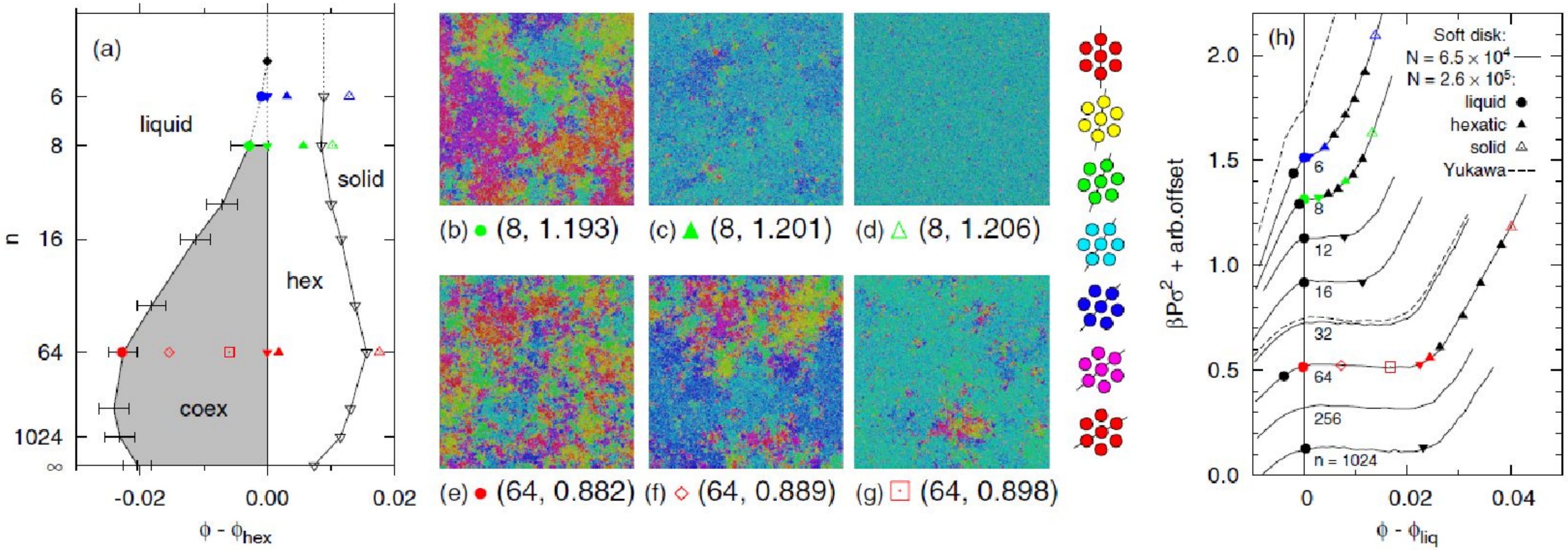
There are two possibilities:

1: $T_m < T_{MF}$. The system melts via two continuous transitions of the Kosterlitz–Thouless type with the unbinding of dislocation pairs.
2: $T_m > T_{MF}$. The system melts via a first-order transition because of the existence of third-order terms in the Landau expansion.

Possible scenarios: grain boundaries (S.T. Chui, Phys. Rev. Lett. 48, 933 (1982); Phys. Rev. B 28, 178 (1983)); dissociation of disclination quadrupoles (V.N. Ryzhov, Zh. Eksp. Theor. Phys. 100, 1627 (1991)), etc…

Third scenario of 2D melting: 2D soft spheres system $1/r^n$ (E.P. Bernard and W. Krauth, Phys. Rev. Lett. 107, 155704 (2011); S.C. Kapfer and W. Krauth, Phys. Rev. Lett. 114, 035702 (2015))

n≤6 – BKTHNY scenario (two continuous BKT-type transitions)
n>6 - continuous BKT-type transition from solid to hexatic phase and first-order transition from hexatic to isotropic liquid



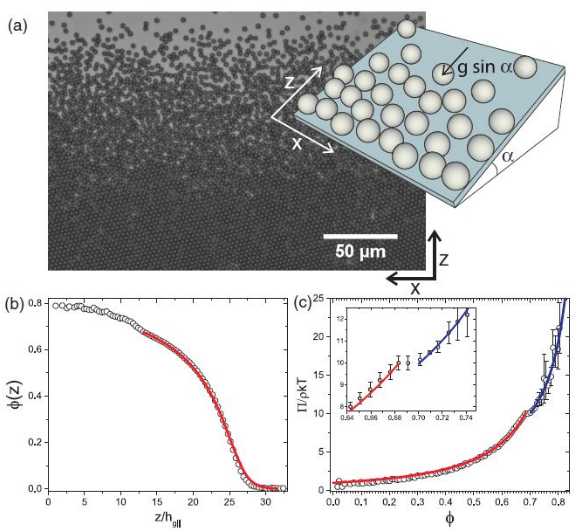
Possible mechanism???

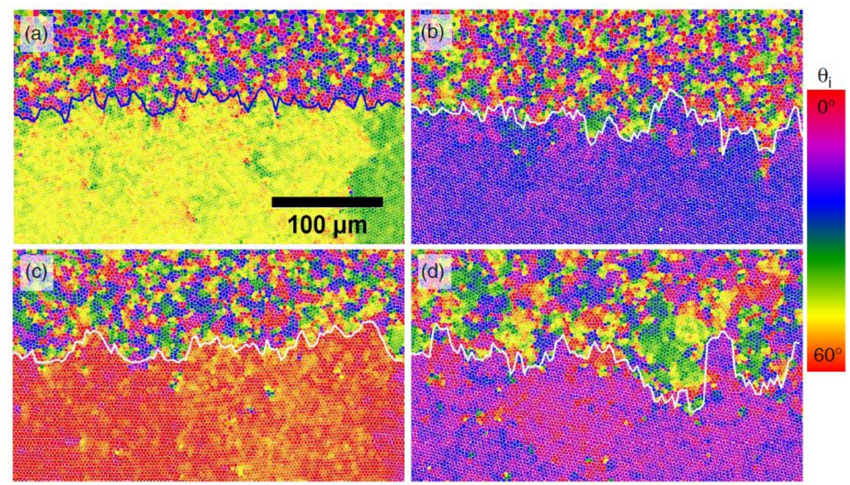
First-order liquid-hexatic transition in hard disk system - experiment

PRL **118,** 158001 (2017) PHYSICAL REVIEW LETTERS week ending 14 APRIL 2017

Two-Dimensional Melting of Colloidal Hard Spheres

Alice L. Thorneywork, Joshua L. Abbott, Dirk G. A. L. Aarts, and Roel P. A. Dullens*



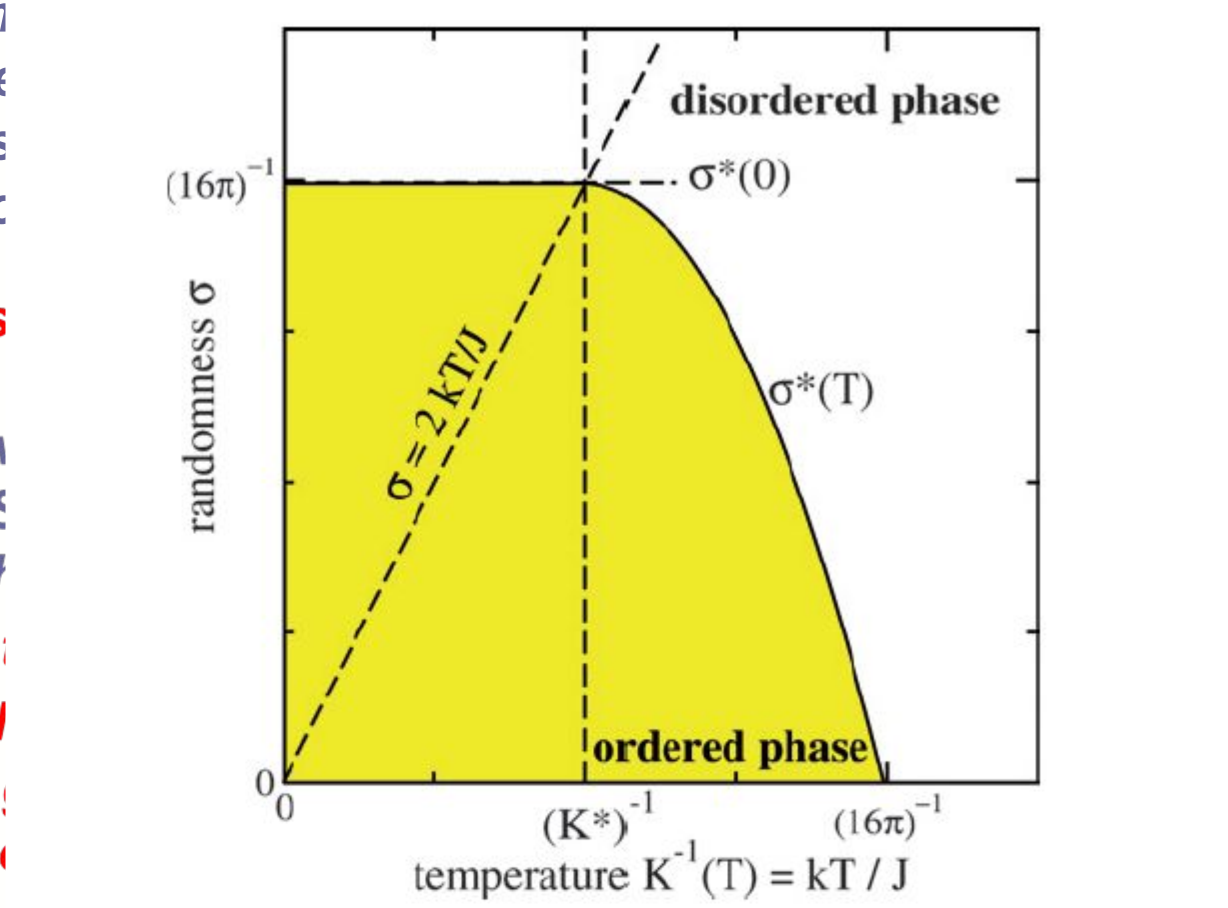


The liquid-hexatic transition is found to be first order, with a coexistence region of $\phi \approx 0.68$–0.70.

The hexatic phase is observed for $0.70 < \phi < 0.73$, *with the hexatic-crystal transition at* $\phi \approx 0.73$.

Theoretical background: Influence of random pinning on the phase diagram

In experim *dsorption on an inte* *on solid substrates* *rder due to some ro*



As it was *e melting scenario* *R. Nelson, Phys. Re* *, J. Phys. C-Solid S* *and H. A. Fertig, Pl* *range of the hexa* *hile T_i is predicted* *ases with increasin* *e can be establish*

Theoretical background – melting criteria: order parameters and correlation functions

Bond orientational and translational order parameters

$$\Psi_6(\mathbf{r_i}) = \frac{1}{n(i)} \sum_{j=1}^{n(i)} e^{in\theta_{ij}} \qquad \psi_6 = \frac{1}{N} \left\langle \left\langle \left| \sum_i \Psi_6(\mathbf{r}_i) \right| \right\rangle \right\rangle_{rp} \qquad \psi_T = \frac{1}{N} \left\langle \left\langle \left| \sum_i e^{i\mathbf{G}\mathbf{r}_i} \right| \right\rangle \right\rangle_{rp}$$

The orientational correlation function $G_6(r)$

The translational correlation function $G_T(r)$

$$G_6(r) = \left\langle \frac{\langle \Psi_6(\mathbf{r}) \Psi_6^*(\mathbf{0}) \rangle}{g(r)} \right\rangle_{rp}$$

$$G_T(r) = \left\langle \frac{< \exp(i\mathbf{G}(\mathbf{r}_i - \mathbf{r}_j)) >}{g(r)} \right\rangle_{rp}$$

$$G_T(r) = \begin{cases} r^{-\eta_T(T)}, & T \leq T_m \\ e^{-r/\xi_T(T)}, & T > T_m \end{cases}$$

$$G_6(r) = \begin{cases} r^{-\eta_6(T)}, & T \leq T_i \\ e^{-r/\xi_6(T)}, & T > T_i \end{cases}$$

Instability parameters are determined from the equations

$$\eta_T(T_m) = 1/3$$

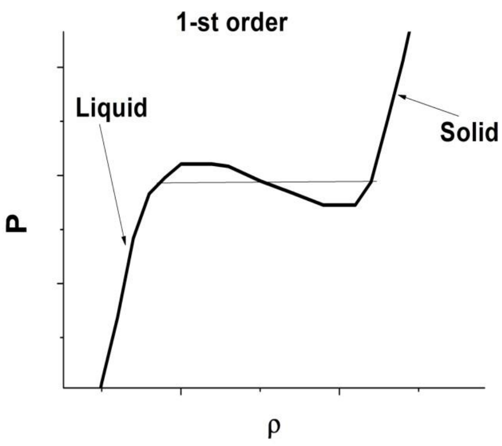
$$\eta_6(T_i) = 1/4$$

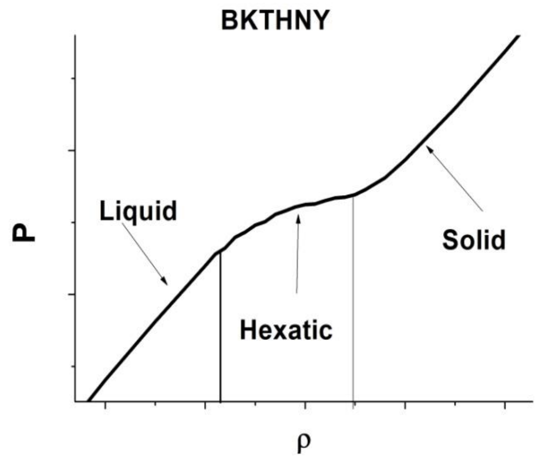
Equations of states for three melting scenarios of 2D systems (V.N. Ryzhov, E.E. Tareyeva, Yu.D. Fomin, E.N. Tsiok, Physics Uspekhi 60, 857 (2017)).

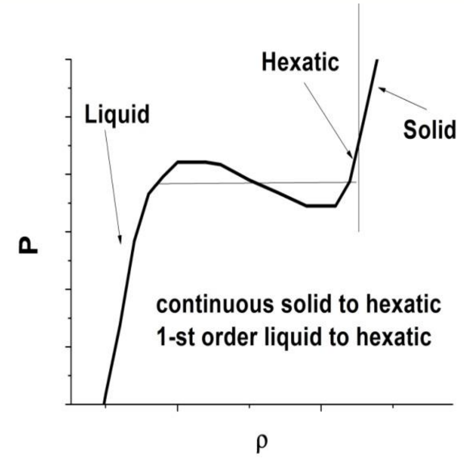
First-order transition

BKTHNY scenario

First-order liquid-hexatic and continuous hexatic-solid transition



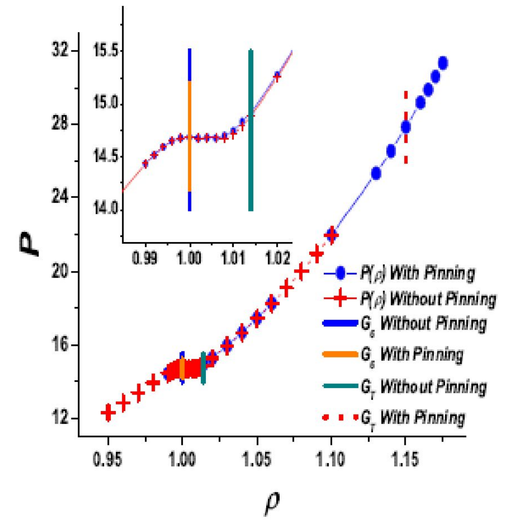


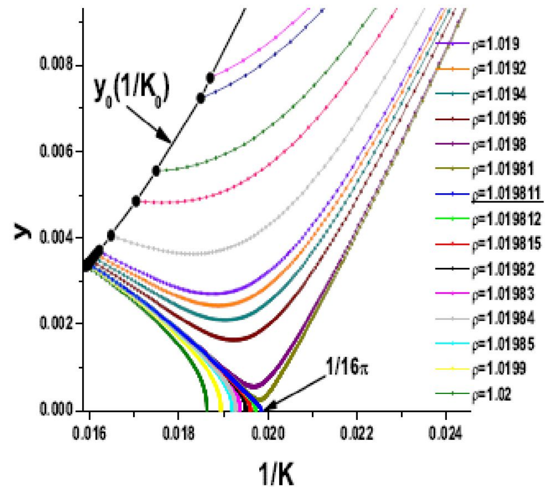


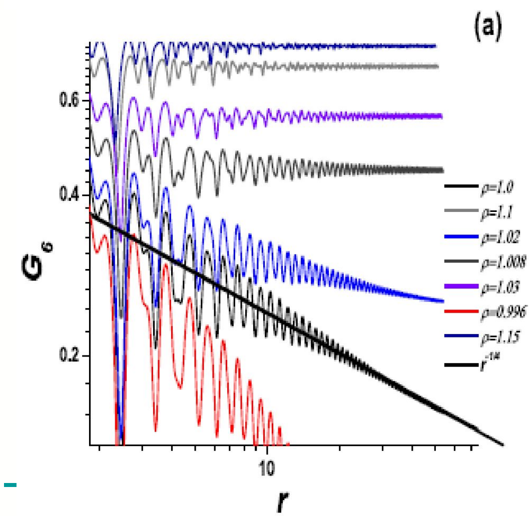
$$K = \frac{8}{\sqrt{3}\rho k_B T} \frac{(\lambda + \mu)\mu}{\lambda + 2\mu} = 16\pi.$$

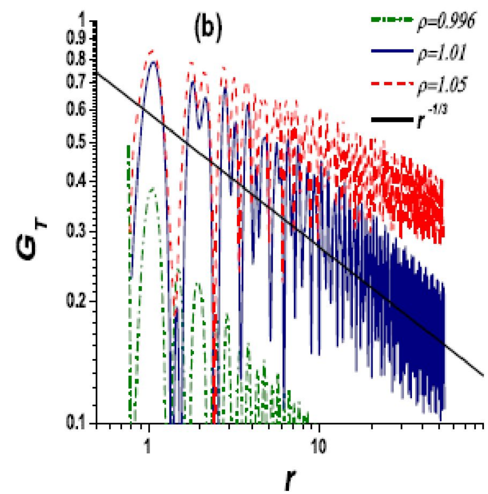
BKTHNY criterion

Melting of 2D soft spheres $1/r^n$, *n=12 (E. A. Gaiduk, Yu. D. Fomin, E. N. Tsiok, and V. N. Ryzhov, arXiv: 1812.02007)*









Melting parameters at T=1

$\rho_{TCF} = 1.014$

$\rho_{rg} = 1.02$

$\rho_{MF} = 1.014$

$\rho_l = 0.998;\ \rho_{hp} = 1.006$

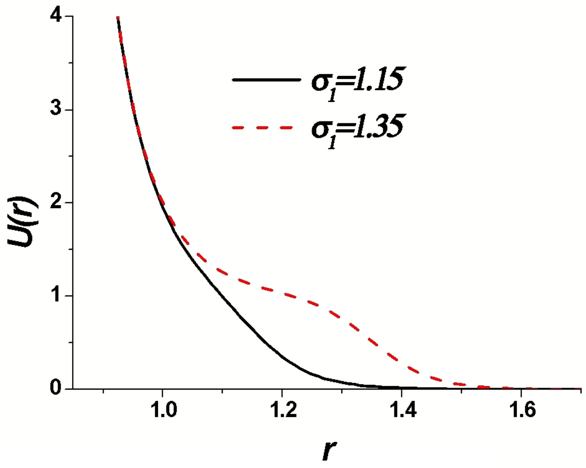
S.C. Kapfer and W. Krauth, PRL 114, 035702 (2015)

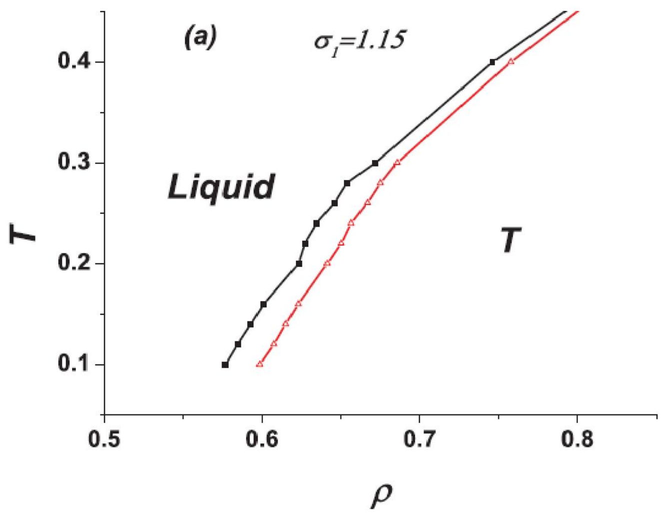
ρ_S=1.015

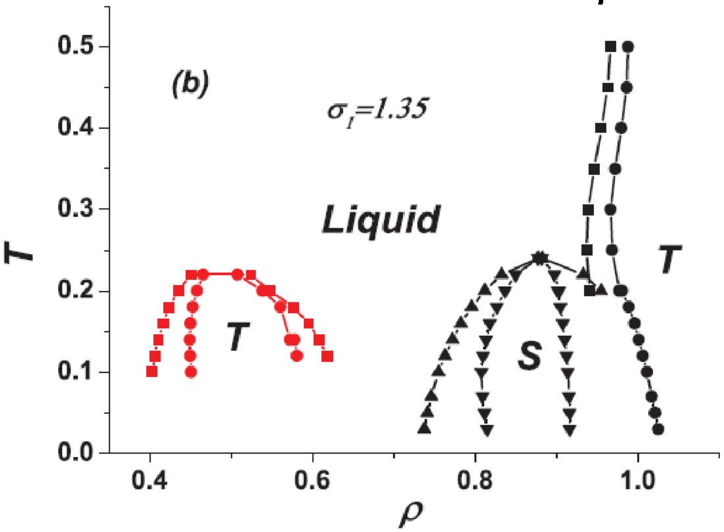
$\rho_l = 0.998;\ \rho_{hp} = 1.005$

Phase diagram of the 2D core-softened system – effect of the potential softness

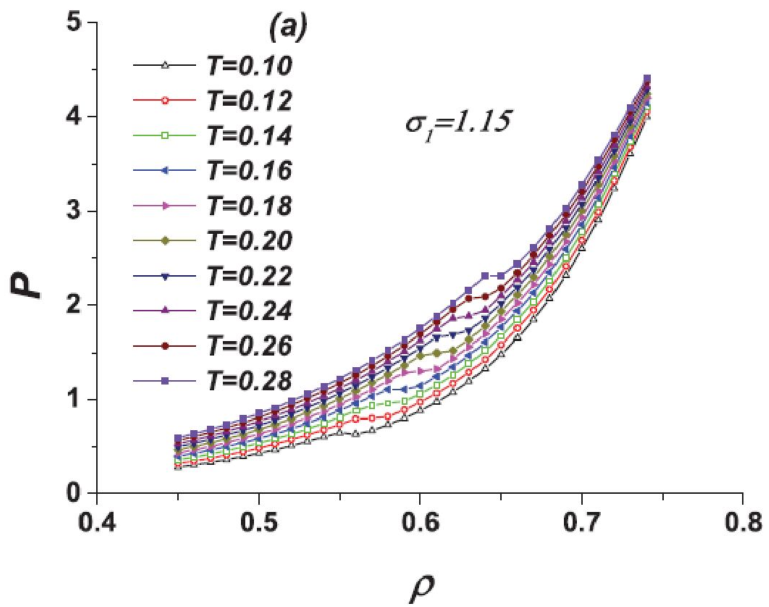
Helmholtz free energy calculations for different phases and a common tangent to them (D. Frenkel and B. Smit, *Understanding Molecular Simulation* (Academic, New York, 2002))

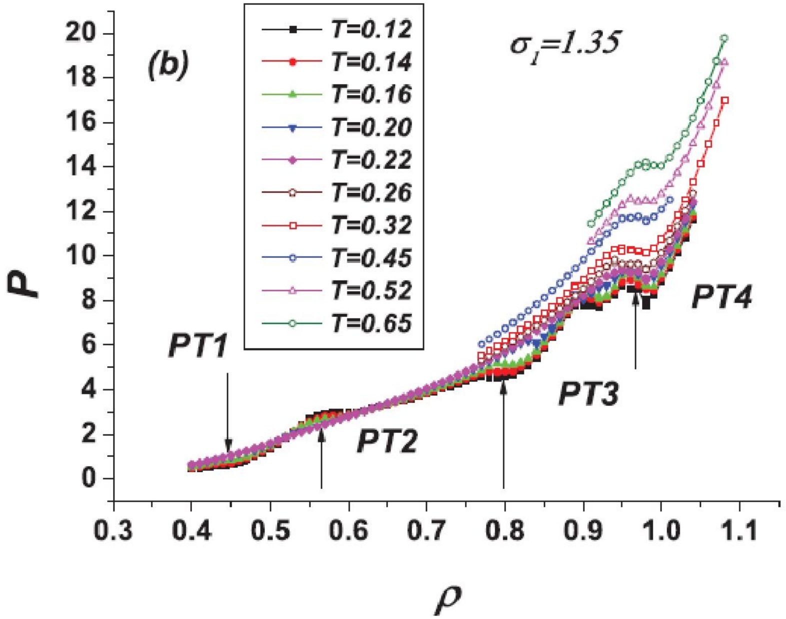






Melting transition in 2D core-softened system - effect of the potential softness



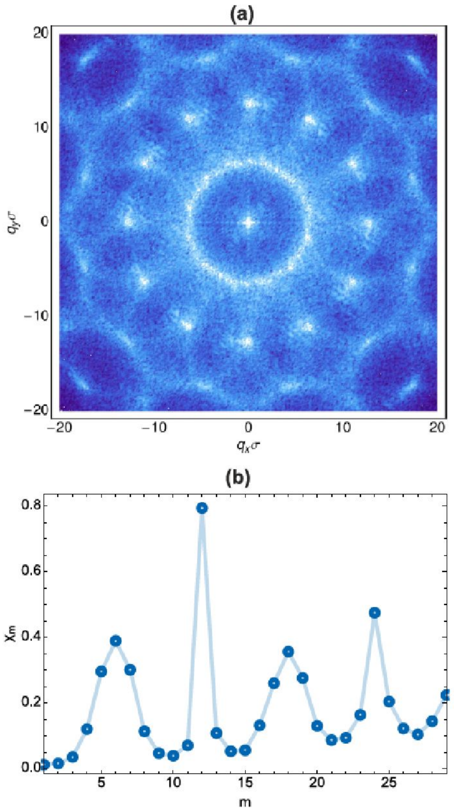


For σ=1.15 one liquid-solid first order transition ???

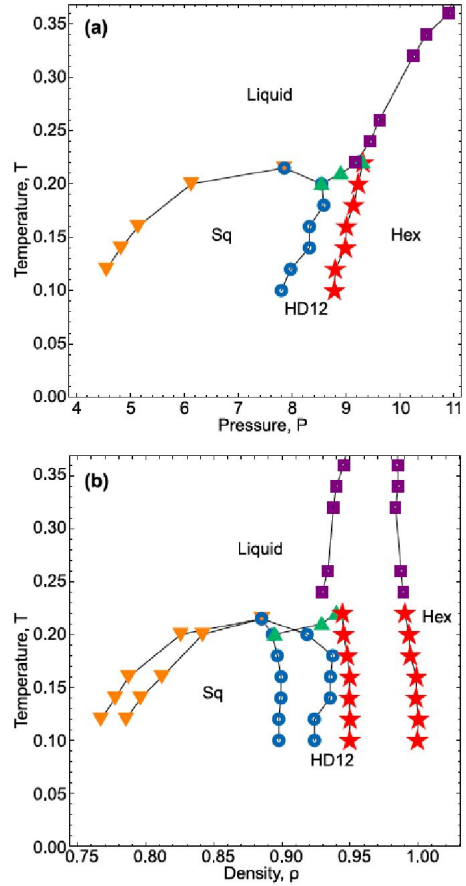
For σ=1.35 there are several transitions, corresponding to the phase diagram at the previous slide.

However, more detailed study is necessary!

Melting transition in core-softened system with s=1.35 at high densities - dodecagonal quasicrystal (N. P. Kryuchkov, S. O. Yurchenko, Y. D. Fomin, E. N. Tsiok and V. N. Ryzhov, Soft Matter 14, 2152 (2018))

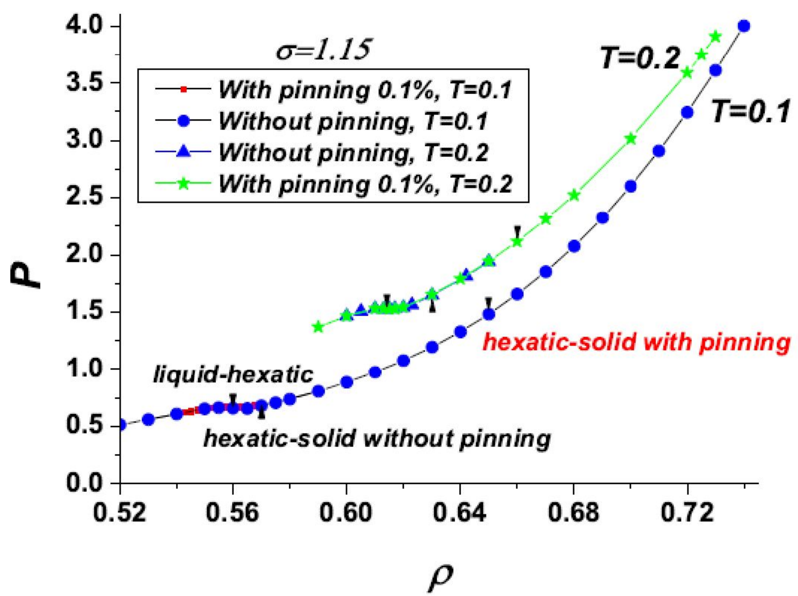


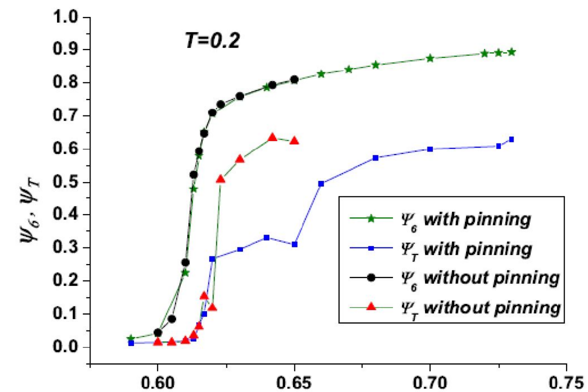
(a) the form factor S(q) and (b) averaged order parameter χ_m calculated for the structure obtained by MD simulations at T = 0.12 and ρ= 0.94

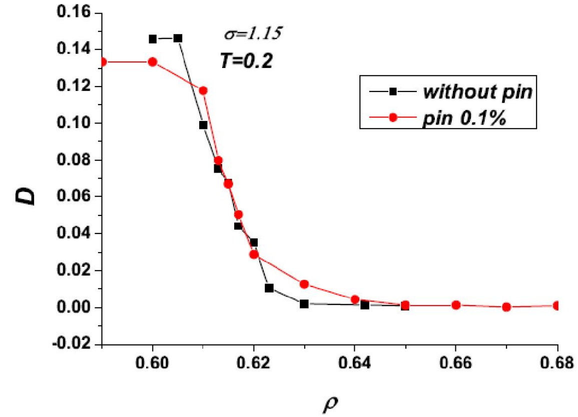


Phase diagram of the system in the (a) P-T and (b) ρ-T plane

First-order liquid-hexatic and continuous hexatic-solid transition (E. N. Tsiok, D. E. Dudalov, Y. D. Fomin, V. N. Ryzhov, Phys. Rev. E 92, 032110 (2015); E. N. Tsiok, Y. D. Fomin, V. N. Ryzhov, Physica A 490, 819–827 (2018); V.N. Ryzhov, E.E. Tareyeva, Yu.D. Fomin, E.N. Tsiok, Physics Uspekhi 60, 857 (2017))).

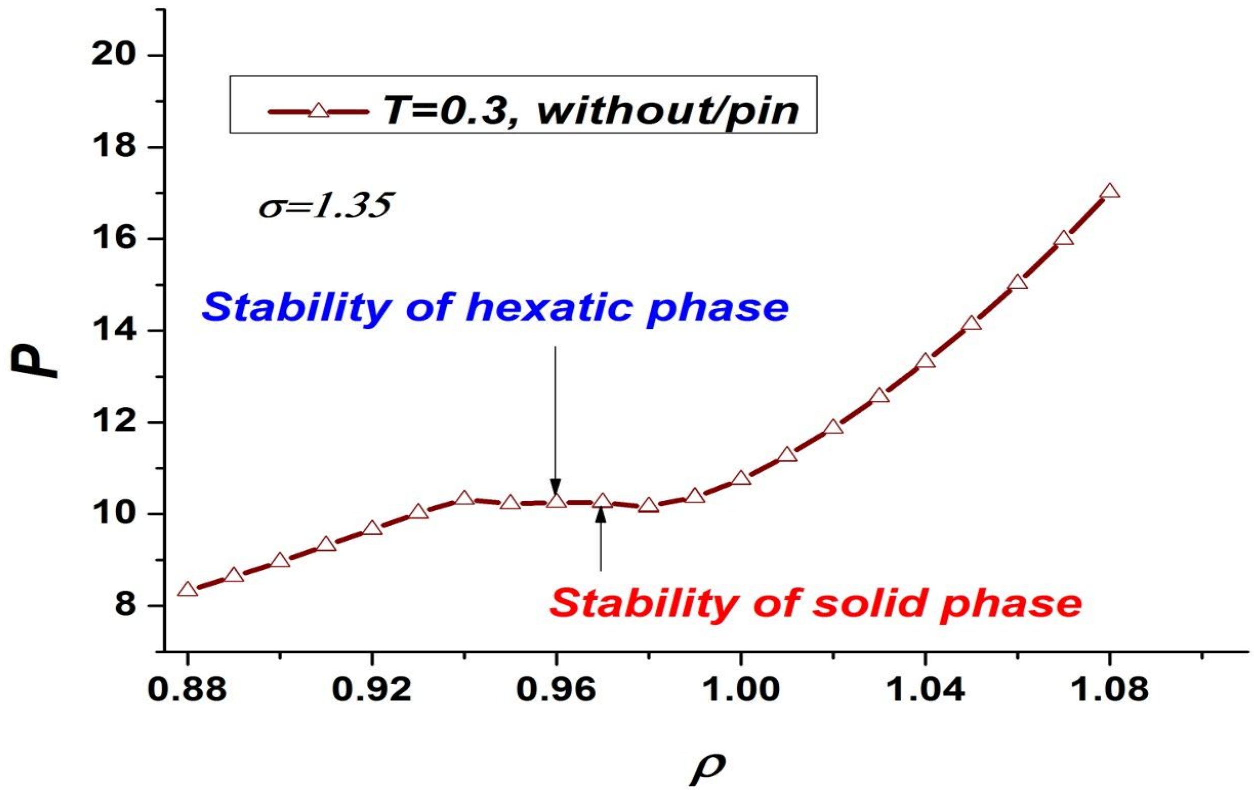






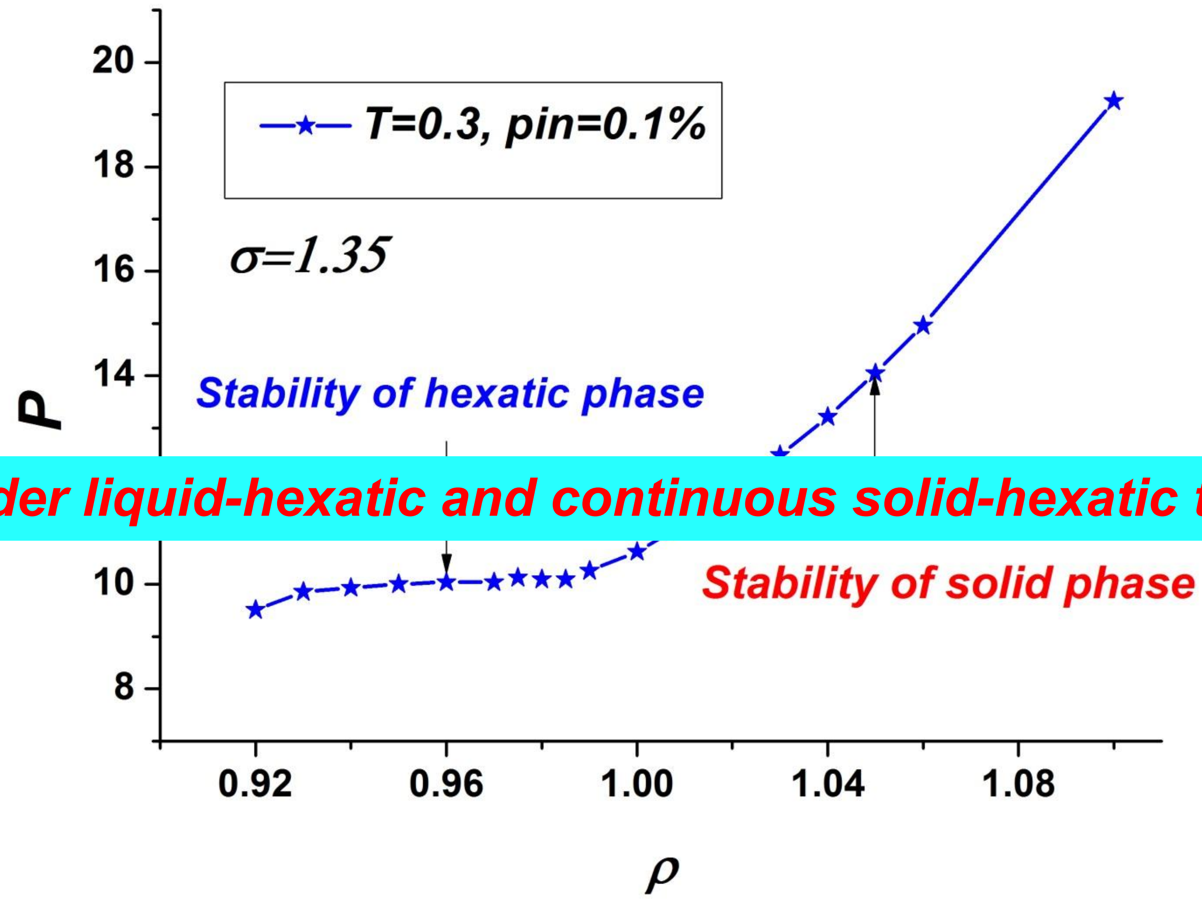
Melting transition in core-softened system for σ=1.15 without and with random pinning:
first—order liquid-hexatic and continuous hexatic-solid transitions without and with pinning

Melting transition in core-softened system with σ=1.35 at high densities without pinning (E. N. Tsiok, D. E. Dudalov, Y. D. Fomin, V. N. Ryzhov, Phys. Rev. E 92, 032110 (2015); V.N. Ryzhov, E.E. Tareyeva, Yu.D. Fomin, E.N. Tsiok, Physics Uspekhi 60, 857 (2017)).



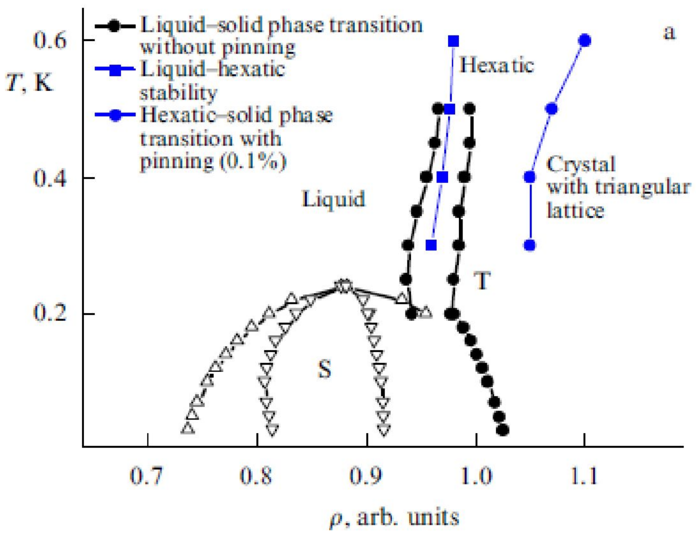
First-order transition!

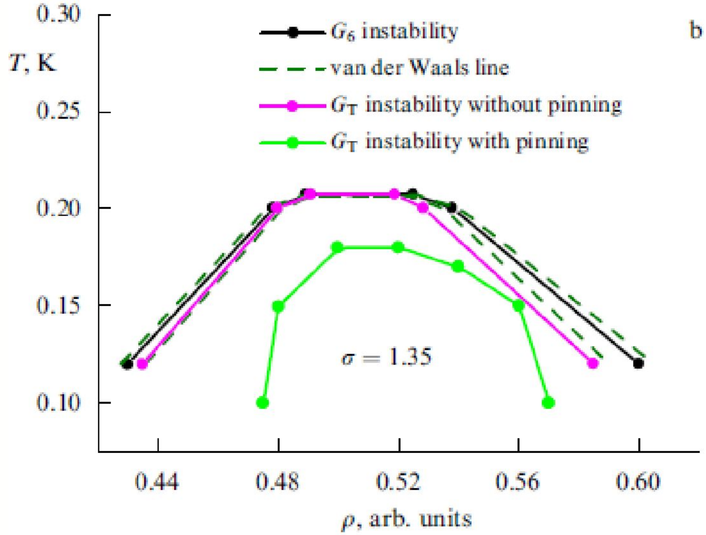
Melting transition in core-softened system with σ=1.35 at high densities with random pinning

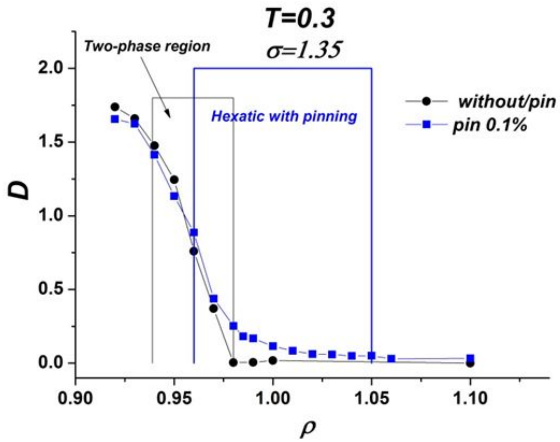


First-order liquid-hexatic and continuous solid-hexatic transitions

Melting transition in core-softened system with s=1.35 at high densities with random pinning (E. N. Tsiok, D.E. Dudalov, Yu. D. Fomin, and V. N. Ryzhov, Phys. Rev. E 92, 032110 (2015); V.N. Ryzhov, E.E. Tareyeva, Yu.D. Fomin, E.N. Tsiok, Physics Uspekhi 60, 857 (2017))

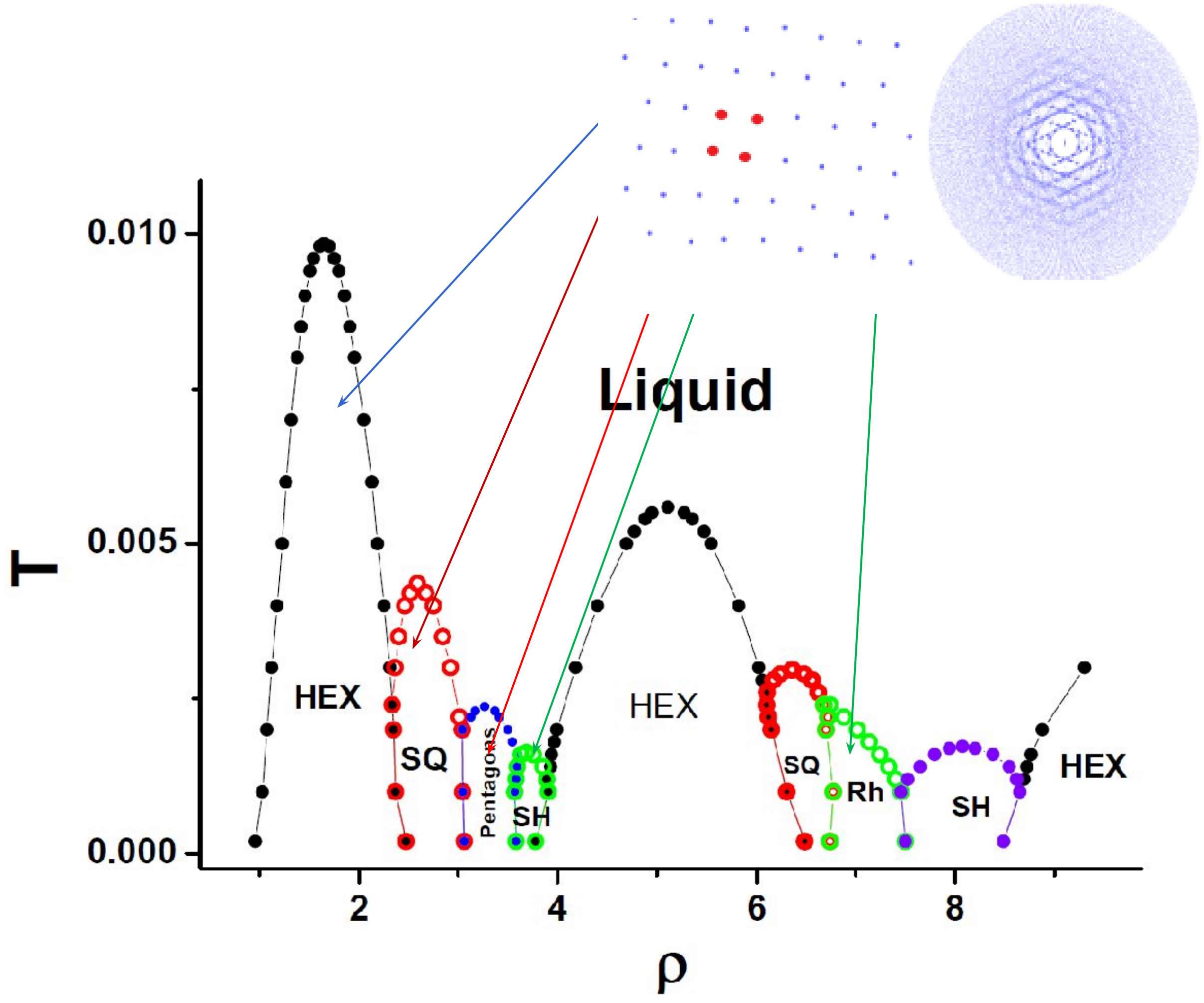




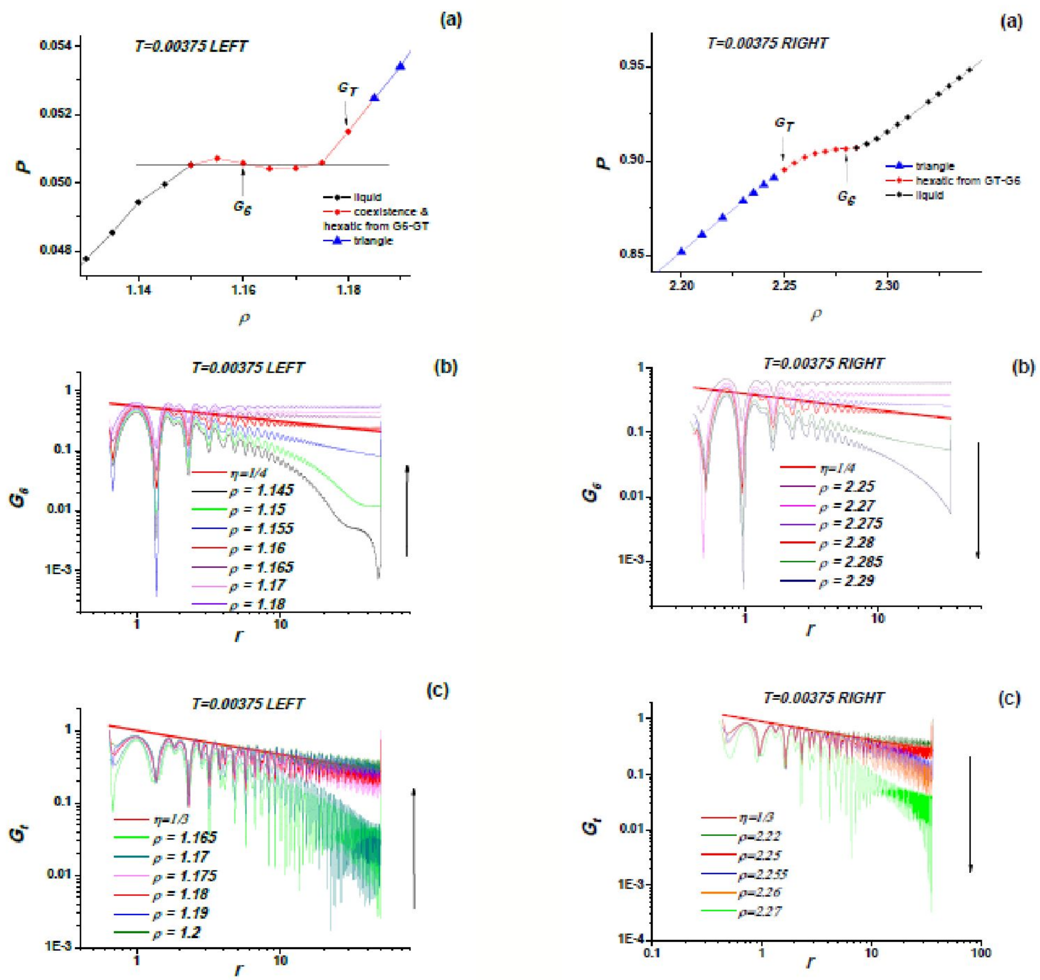


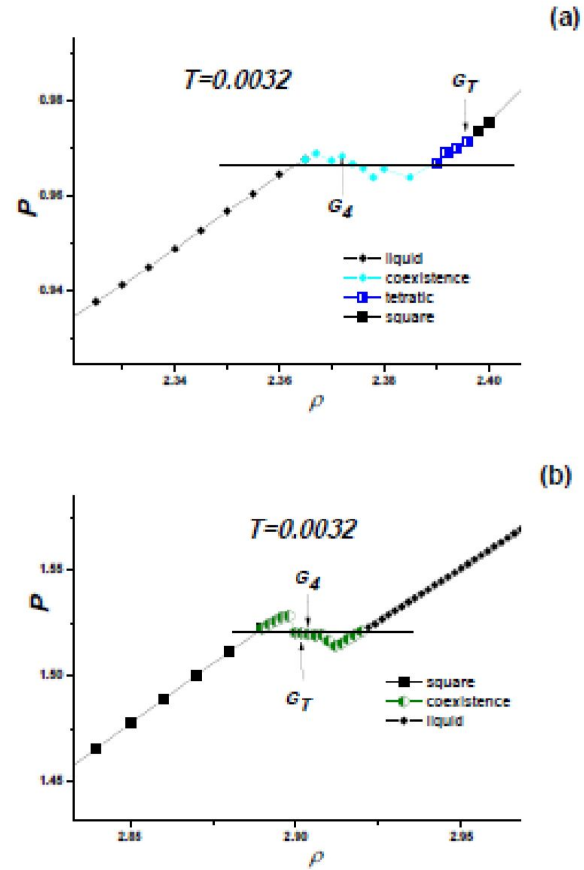
First-order liquid-hexatic and continuous solid-hexatic transitions

Phase diagram of the 2D Herzian disks (a=5/2) without random pinning (Yu. D. Fomin, E. A. Gaiduk, E. N. Tsiok, and V. N. Ryzhov, Molecular Physics, DOI: 10.1080/00268976.2018.1464676 (2018))



Phase diagram of the 2D Herzian disks (a=5/2) without random pinning (Yu. D. Fomin, E. A. Gaiduk, E. N. Tsiok, and V. N. Ryzhov, Molecular Physics, DOI: 10.1080/00268976.2018.1464676 (2018))

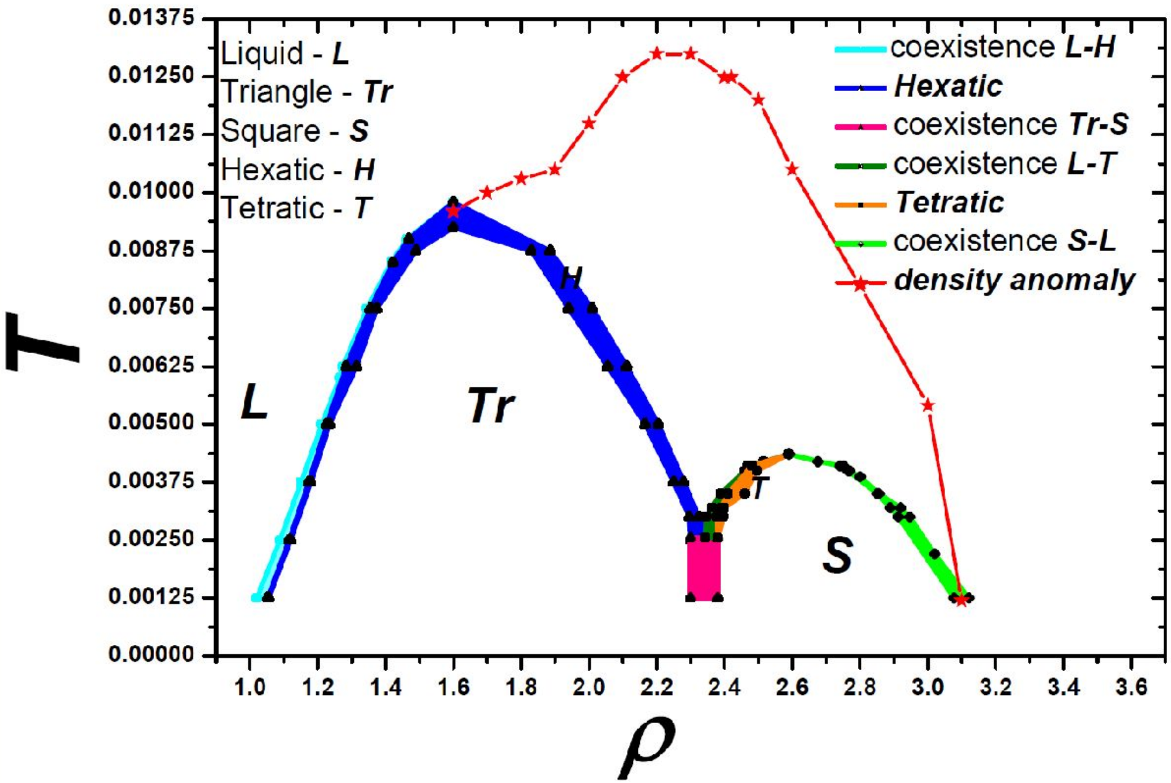


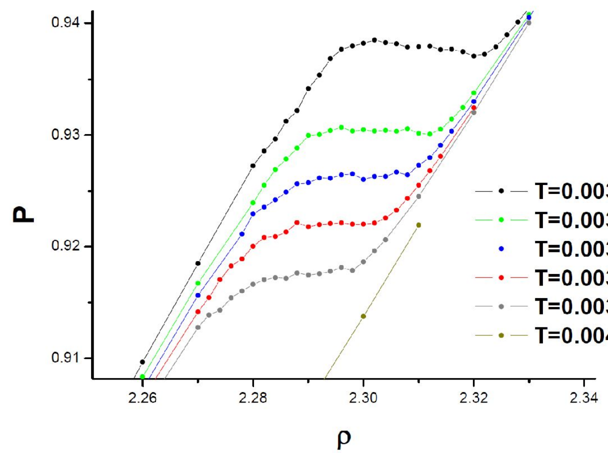


Square phase

low-density triangular phase

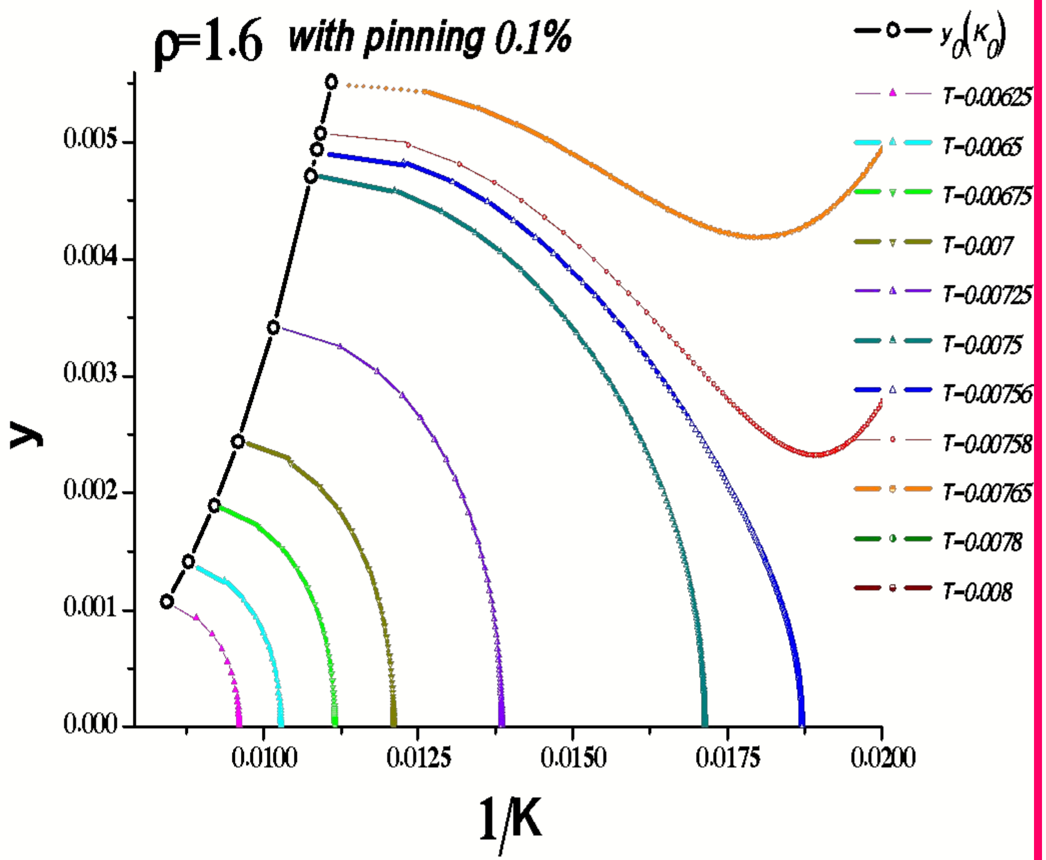
Phase diagram of the 2D Herzian disks (a=5/2) without random pinning (Yu. D. Fomin, E. A. Gaiduk, E. N. Tsiok, and V. N. Ryzhov, Molecular Physics, DOI: 10.1080/00268976.2018.1464676 (2018))





T = 0.0034 and ρ = 2.296 is a tricritical point of the system

Solution of renormalization group equations



$$K = \frac{8}{\sqrt{3}\rho k_B T}\frac{(\lambda+\mu)\mu}{\lambda+2\mu} = 16\pi.$$

$$p_d = \frac{16\sqrt{3}\pi^2}{K-8\pi} I_0\left(\frac{K}{8\pi}\right)\exp\left(\frac{K}{8\pi}\right)\exp\left(\frac{-2E_c}{k_B T}\right)$$

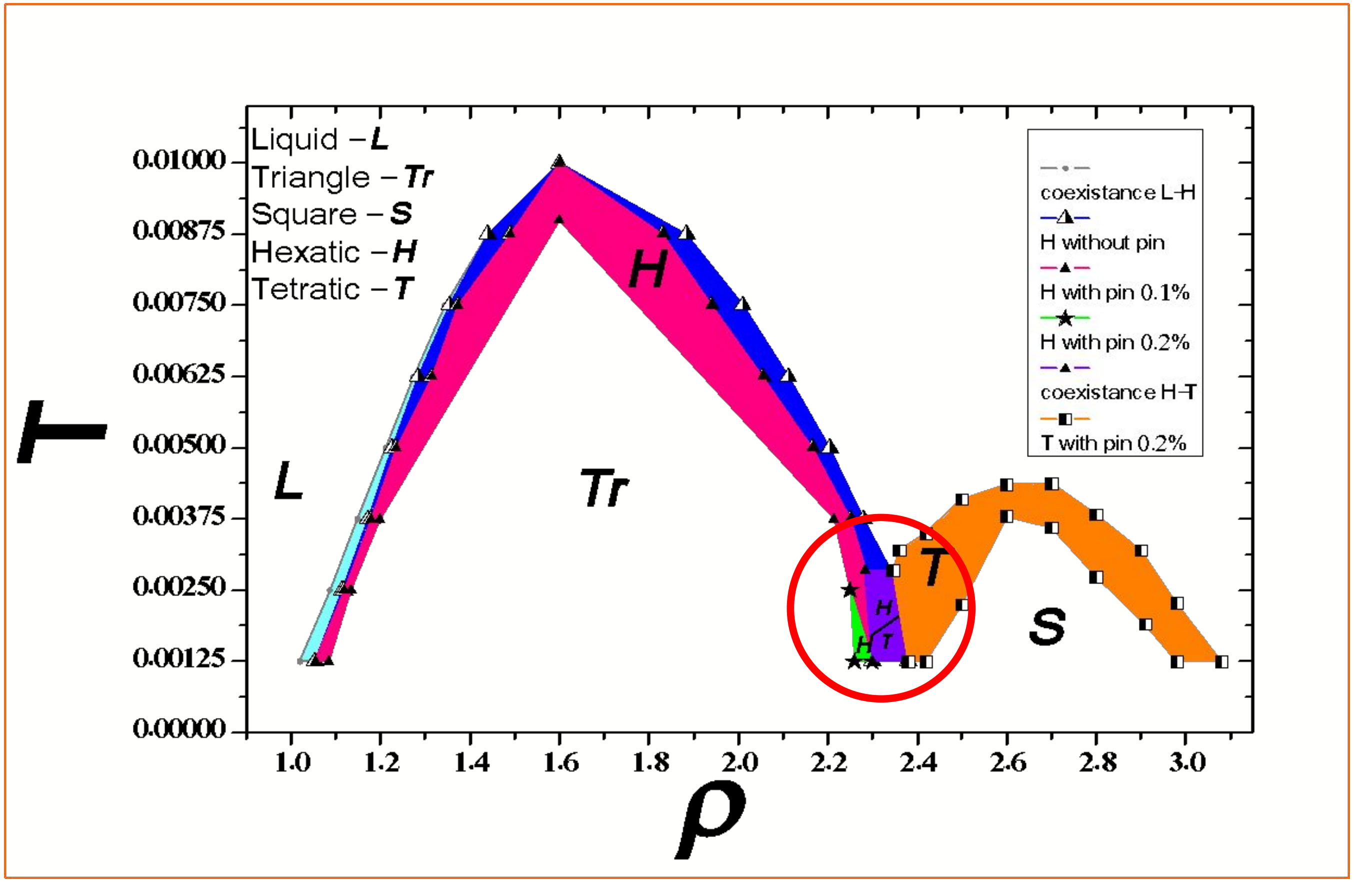
$$\frac{dK^{-1}(l)}{dl} = \frac{3}{4}\pi y^2(l) e^{\frac{K(l)}{8\pi}}\left[2I_0\left(\frac{K(l)}{8\pi}\right) - I_1\left(\frac{K(l)}{8\pi}\right)\right]$$

$$\frac{dy(l)}{dl} = \left(2 - \frac{K(l)}{8\pi}\right)y(l) + 2\pi y^2(l) e^{\frac{K(l)}{16\pi}} I_0\left(\frac{K(l)}{8\pi}\right)$$

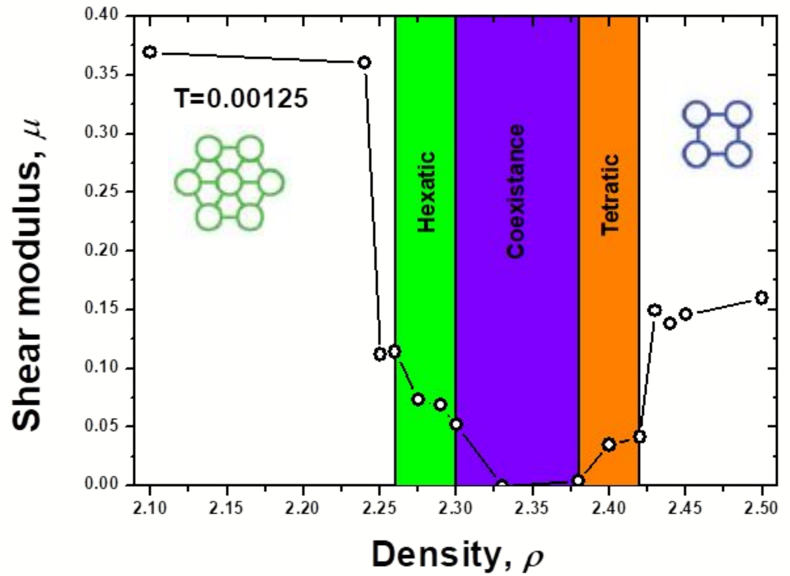
λ and μ - elastic moduli,
E_c – core energy of dislocation,
y –fugacity

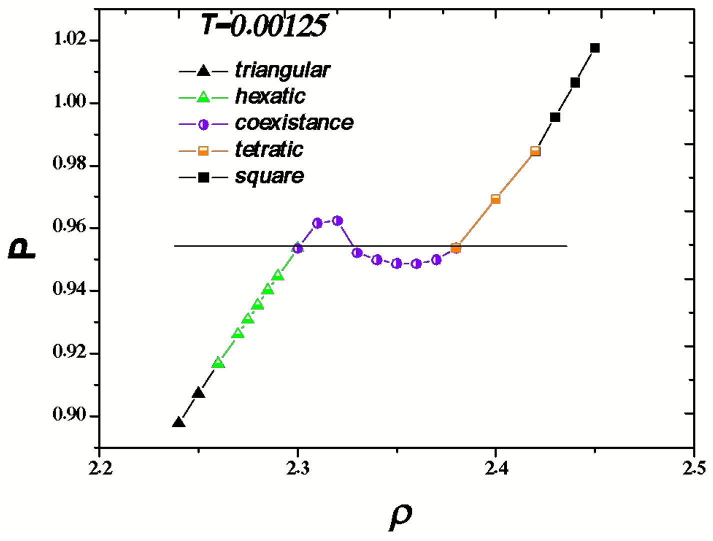
$$y = \exp[-E_c/(k_B T)].$$

Phase diagram of the 2D Herzian spheres (a=5/2) in the presence of random pinning – reentering hexatic and tetratic phases



Behavior of the shear modulus μ between the triangle and square crystals in the presence of the random pinning





Continuous BKT transition from triangle crystal to hexatic phase, first order transition between hexatic to tetratic phases, continuous BKT transition from tetratic to square crystal.

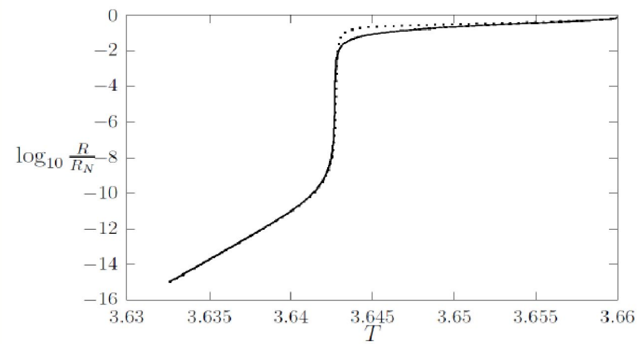
Possible mechanism of first-order BKT transition – thin superconducting films (V. N. Ryzhov, E. E. Tareyeva, Phys. Rev. B 49, 6162 (1994); D. Y. Irz, V. N. Ryzhov, E. E. Tareyeva, Phys. Rev. B 54, 3051 (1996)).

Potential between the topological defects (vortices).

$$\Phi(r_{ij}) = \frac{\varphi_0^2}{8\pi\Lambda}\left[H_0\left(\frac{r_{ij}}{\Lambda}\right) - Y_0\left(\frac{r_{ij}}{\Lambda}\right)\right]$$

$$\Phi(r_{ij}) \approx -\frac{\varphi_0^2}{4\pi^2\Lambda}\ln\left(\frac{r_{ij}}{\Lambda}\right) \qquad r_{ij} \ll \Lambda$$

$$\Phi(r_{ij}) \approx \frac{\varphi_0^2}{4\pi^2 r_{ij}} \qquad r_{ij} \gg \Lambda$$

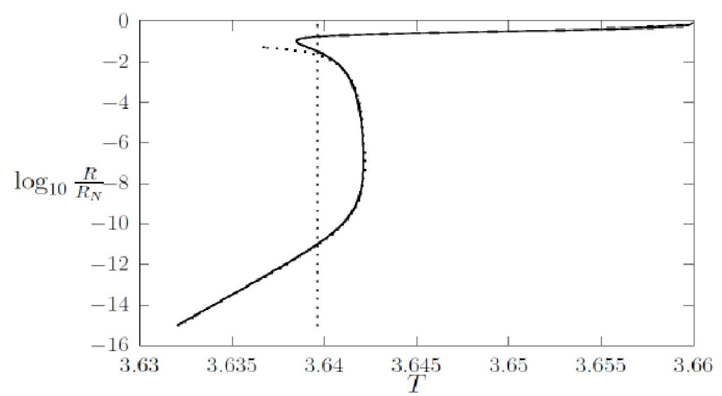


Large defect core energy – continuous transition

Defect core energy

$$\varepsilon = \pi r_0^2 \xi^2 \left(\frac{H_c^2}{8\pi}\right) + \frac{\varphi_0^2}{16\pi\Lambda d}\left(H_0\left(\frac{\xi}{\Lambda}\right) - Y_0\left(\frac{\xi}{\Lambda}\right)\right)$$

Small defect core energy – first-order transition



Melting scenarios in two-dimensions: Landau and BKTHNY theories of liquid-hexatic transition

Order parameter $\psi_6(\mathbf{r}) = |\psi_6(\mathbf{r})| e^{6i\theta(\mathbf{r})}$

$$\mathcal{F}[\psi(\mathbf{r})] = \frac{1}{2}|\nabla\psi(\mathbf{r})|^2 + \frac{r(T)}{2}|\psi|^2 + \frac{u}{4}|\psi|^4 + \cdots \quad r(T) = a(T - T_{MF})$$

BKT liquid-hexatic transition

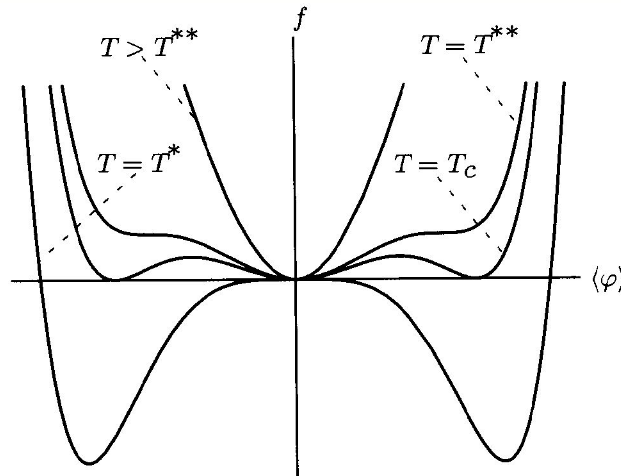
Unbinding of the singular topological defects of the order-parameter phase (disclinations) at T_i - BKT transition. Continuous transition at T_i and at T_{MF}.

What is the mechanism of the first-order liquid-hexatic transition (Landau theory)?

Qualitative scenario of first-order transition between hexatic phase and isotropic liquid.

Interaction of orientational and translational order parameters

$$F[\psi(\mathbf{r}), \rho_G(\mathbf{r})]$$



$$\frac{u}{4}|\psi|^4 + \dots$$

$$\frac{c}{4}|\psi|^2|\rho_G|^2 + \dots$$

Effective Ha **out the translational order parameter**

$$F_{eff}[\psi(\mathbf{r})] = \frac{1}{2}|\nabla\psi(\mathbf{r})|^2 + \frac{r^*(T)}{2}|\psi|^2 + \frac{u^*}{4}|\psi|^4 + \frac{v^*}{6}|\psi|^6 + \frac{h^*}{8}|\psi|^8$$

$$u^* > 0;\ v^* < 0;\ h^* > 0$$

Conclusions

1). In 2D there are three melting scenarios. In our systems melting can occur in accordance with BKTHNY theory, through a first-order phase transition and as a result of two transitions with the intermediate hexatic phase - first-order liquid-hexatic and continuous hexatic-solid transition. The melting scenario drastically depends on the form of the potential.

2). The influence of the random pinning on the phase diagram is investigated. It is shown that pinning transforms the first order melting into two transitions: first-order liquid-hexatic transition and continuous hexatic-solid transition. In the case the two-stage melting pinning drastically widens the hexatic phase.

3). There is no adequate theory of a first-order liquid-hexatic transition. It may be a result of small core energy of disclinations or the interaction between orientational and translational fluctuations.

Thank you for attention

Theoretical background: melting scenarios in two-dimensions: Landau and BKTHNY theories (V. N. Ryzhov et al, Phys. Rev. B 51, 8789 (1995); Physica A 314, 396-404 (2002); Physica A 432 279–286 (2015)).

$$F = \frac{1}{2}\int \sum_{\mathbf{G}} \left[A|\mathbf{G}\times\nabla\rho_{\mathbf{G}}|^2 + B|\mathbf{G}\cdot\nabla\rho_{\mathbf{G}}|^2 + C|\rho_{\mathbf{G}}(\mathbf{G}\cdot\nabla)\rho_{\mathbf{G}}| \right] d^2r +$$

$$+\frac{1}{2}a_T\sum_{\mathbf{G}}|\rho_{\mathbf{G}}|^2 + b_T \sum_{\mathbf{G}_1+\mathbf{G}_2+\mathbf{G}_3=0} \rho_{\mathbf{G}_1}\rho_{\mathbf{G}_2}\rho_{\mathbf{G}_3} + O(\rho^4).$$

Dislocation unbinding temperature T_m.
The modulus of the order parameter vanishes at temperature T_{MF} if the free energies of the liquid and solid phases are equal.

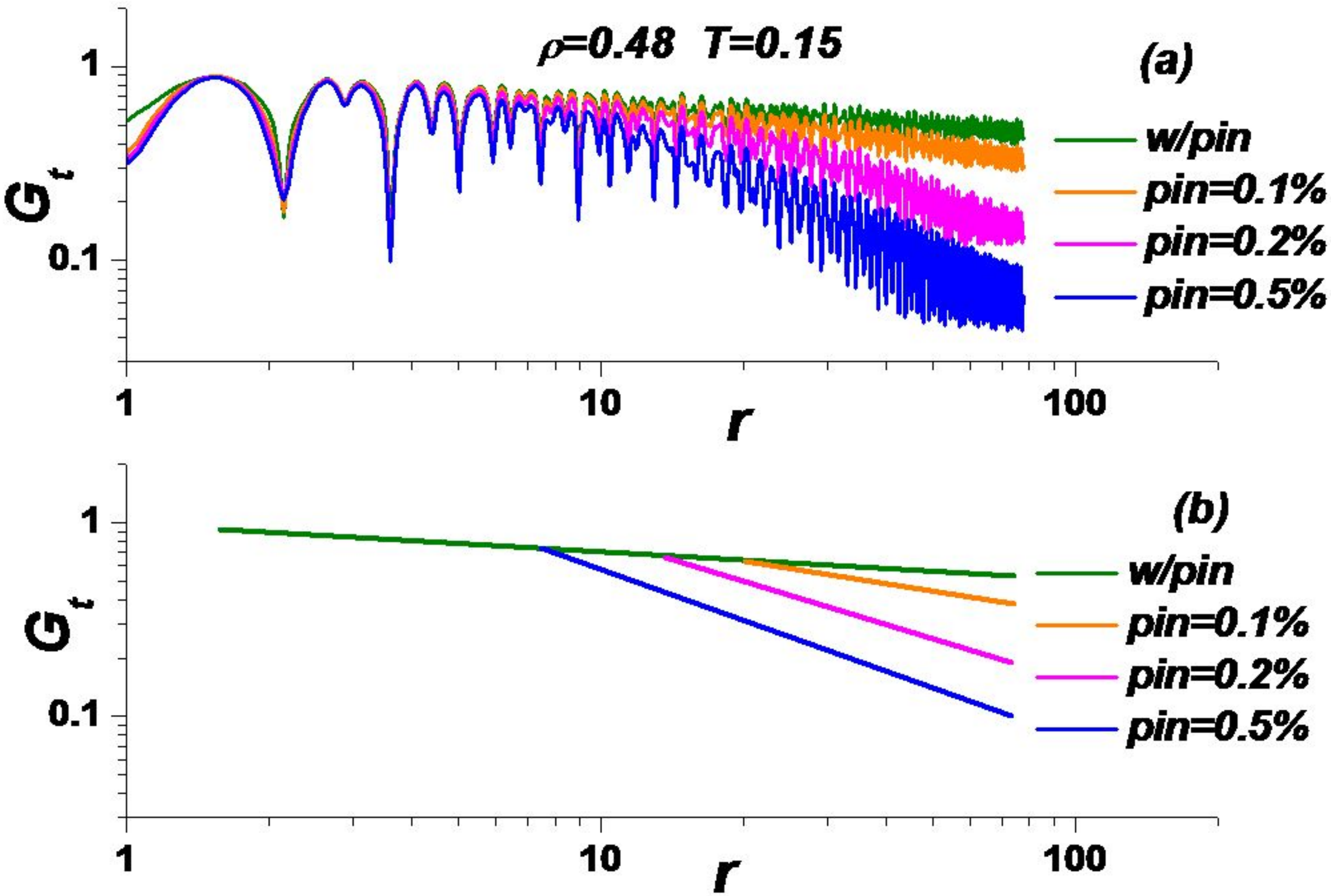
There are two possibilities:

1: $T_m < T_{MF}$. The system melts via two continuous transitions of the Berezinskii-Kosterlitz–Thouless type with the unbinding of dislocation pairs.
2: $T_m > T_{MF}$. The system melts via a first-order transition because of the existence of third-order terms in the Landau expansion.

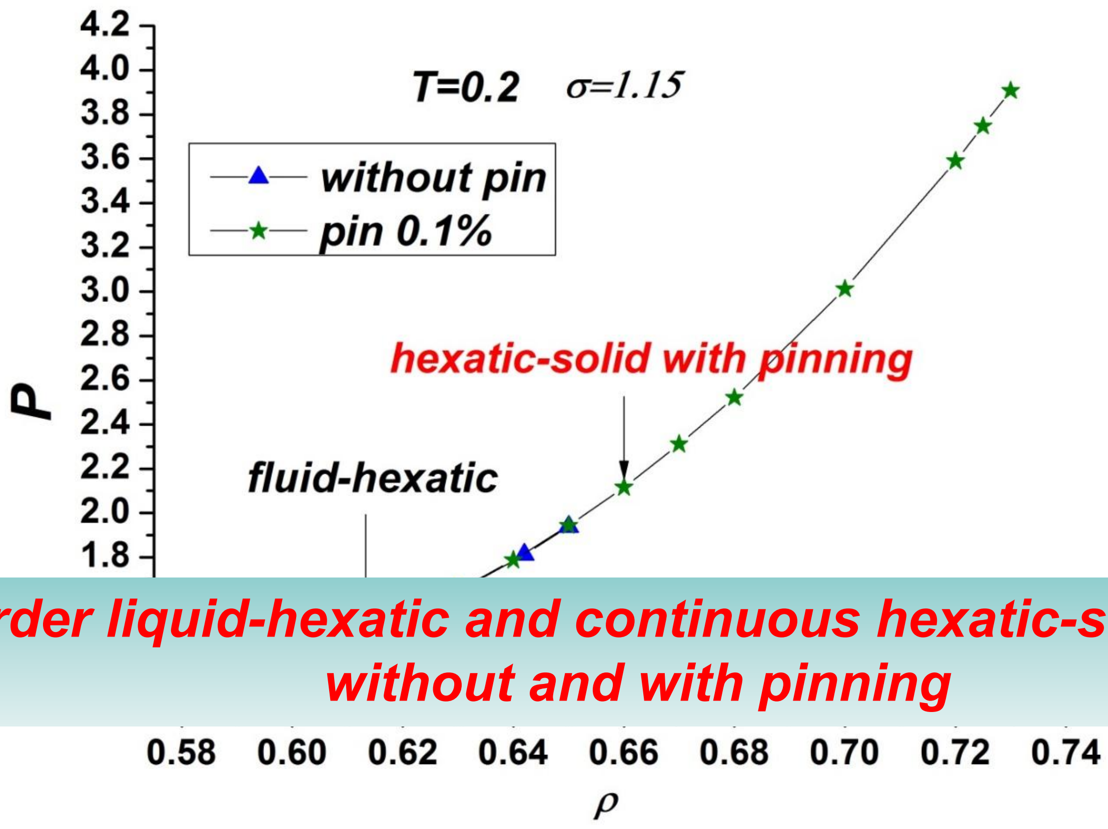
Possible scenarios: grain boundaries (S.T. Chui, Phys. Rev. Lett. 48, 933 (1982); Phys. Rev. B 28, 178 (1983)); dissociation of disclination quadrupoles (V.N. Ryzhov, Zh. Eksp. Theor. Phys. 100, 1627 (1991)), etc…

The instability points can be determined from the behavior of translational and orientational correlation functions

Dependence of translational correlation functions on the random pinning concentrations (E. N. Tsiok, D.E. Dudalov, Yu. D. Fomin, and V. N. Ryzhov, Phys. Rev. E 92, 032110 (2015)).



Melting transition in core-softened system for σ=1.15 without and with random pinning - First-order liquid-hexatic and continuous hexatic-solid transition (E. N. Tsiok, D. E. Dudalov, Y. D. Fomin, V. N. Ryzhov, Phys. Rev. E 92, 032110 (2015); E. N. Tsiok, Y. D. Fomin, V. N. Ryzhov, Physica A 490, 819–827 (2018); V.N. Ryzhov, E.E. Tareyeva, Yu.D. Fomin, E.N. Tsiok, Physics Uspekhi 60, 857 (2017)).



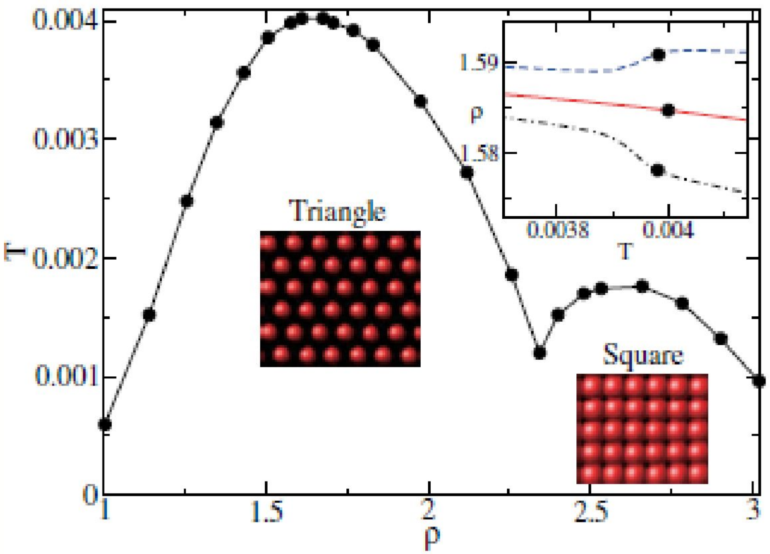
First—order liquid-hexatic and continuous hexatic-solid transitions without and with pinning

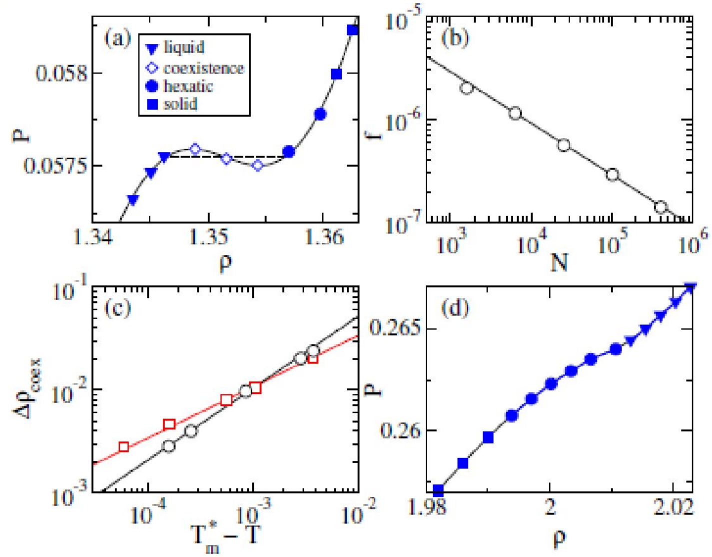
Computer simulations of core softened models – non-triangle structures (some examples)

PRL 117, 085702 (2016) PHYSICAL REVIEW LETTERS week ending 19 AUGUST 2016

Density Affects the Nature of the Hexatic-Liquid Transition in Two-Dimensional Melting of Soft-Core Systems

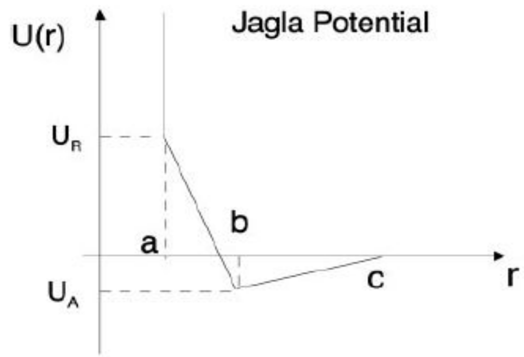
Mengjie Zu, Jun Liu, Hua Tong, and Ning Xu*





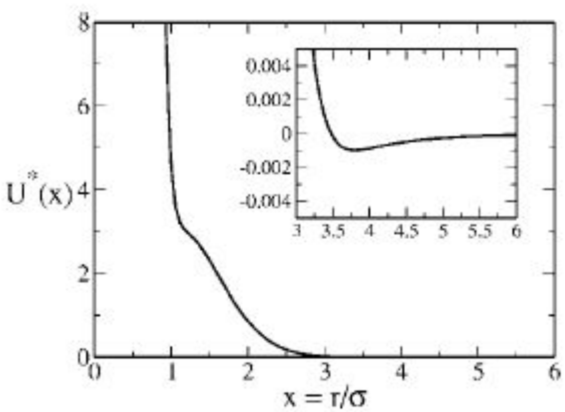
Spherically symmetric two-scale potentials

E. A. Jagla, J. Chem. Phys. 111, 8980 (1999); E. A.
Jagla, Phys. Rev. E 63, 061501 (2001).



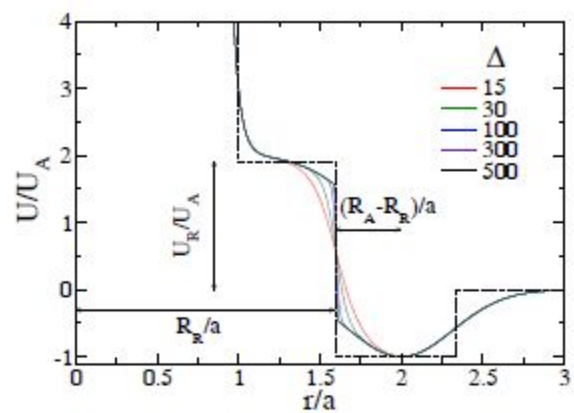
A. B. de Oliveira, P. A. Netz, T. Colla, and M. C. Barbosa, J. Chem. Phys. **124,** 084505 **(**2006).

$$U(r)=4\epsilon\left[\left(\frac{\sigma}{r}\right)^{12}-\left(\frac{\sigma}{r}\right)^{6}\right]+a\epsilon\exp\left[-\frac{1}{c^2}\left(\frac{r-r_0}{\sigma}\right)^{2}\right]$$

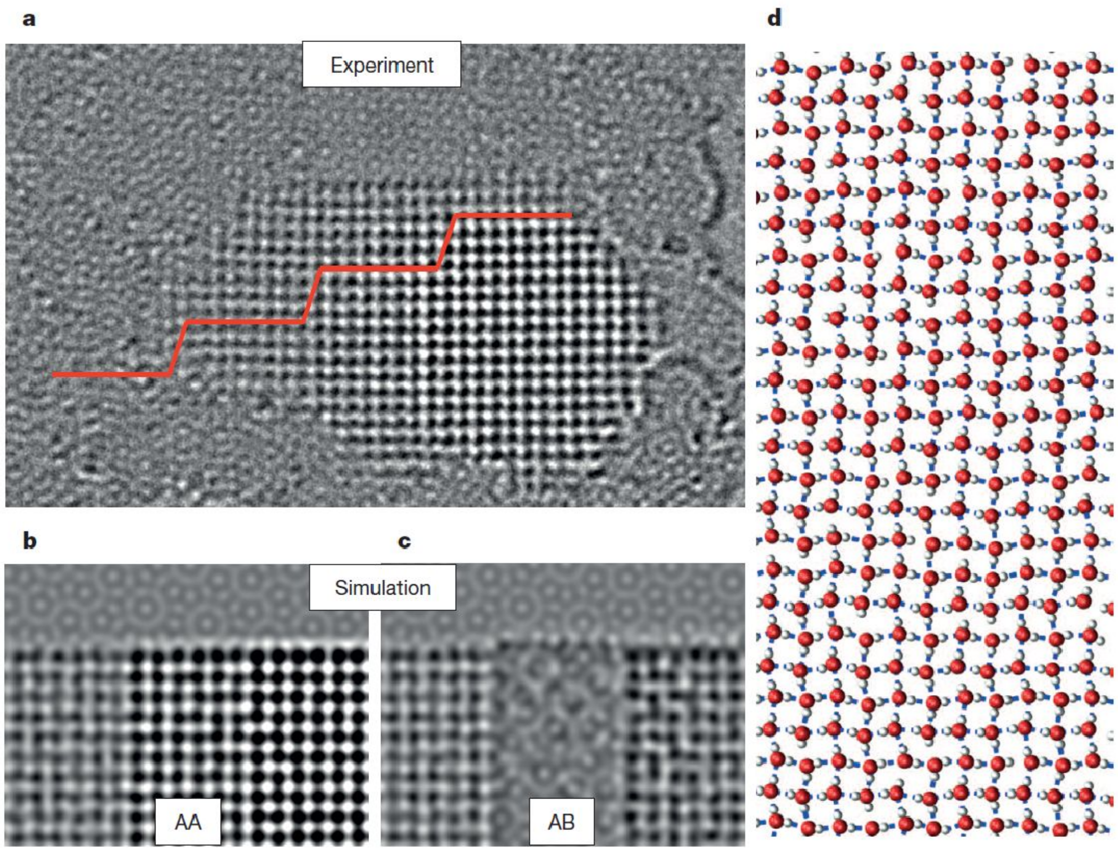


G. Franzese, J. Mol. Liq. 136, 267 2007; Pol Vilaseca and Giancarlo Franzese, J. Chem. Phys., 133, 084507 (2010).

$$U(r)=\frac{U_R}{1+\exp(\Delta(r-R_R)/a)}-U_A\exp\left[-\frac{(r-R_A)^2}{2\delta_A^2}\right]+\left(\frac{a}{r}\right)^{24}$$

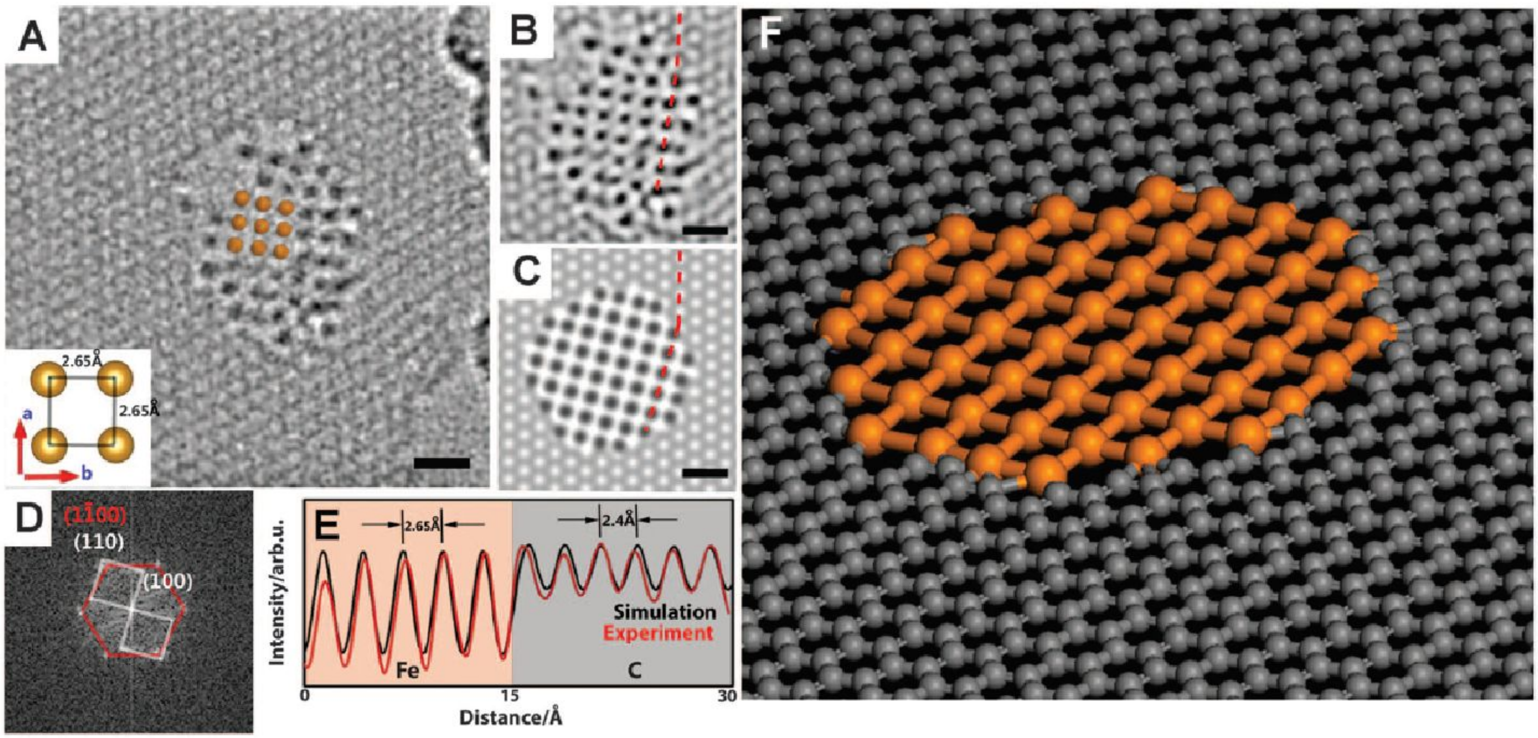


Computer simulations and experimental study of water in slit pores



The nanoconfined between two graphene sheets water at room temperature forms 'square ice'- a phase having symmetry qualitatively different from the conventional tetrahedral geometry of hydrogen bonding between water molecules. Square ice has a high packing density with a lattice constant of 2.83A˚ and can assemble in bilayer and trilayer crystallites ***(G. Algara-Siller, O. Lehtinen, F. C. Wang, R. R. Nair, U. Kaiser, H. A.Wu, A. K. Geim & I. V. Grigorieva, NATURE 5 1 9, 443 (2015)).***

Single-Atom-Thick Iron Membranes Suspended in Graphene Pores (*Jiong Zhao et al., Science* **343**, 1228 (2014))



Melting scenarios in two-dimensions: Landau and BKTHNY theories of liquid-hexatic transition

Order parameter $F_2(\mathbf{r}) = g(r)(1 + f(\mathbf{r}_0))$ $f(\mathbf{r}_0) = \sum_m f_m e^{im\theta}$

Mean-field expansion – transition at T_{MF} $\Delta F = a_6(T - T_c) f_6^2 + b f_6^4$

Fluctuations of the order parameter phase in 2D

$$f_m(\mathbf{r}) = f_m^0 e^{i\phi(\mathbf{r})}$$

BKT liquid-hexatic transition

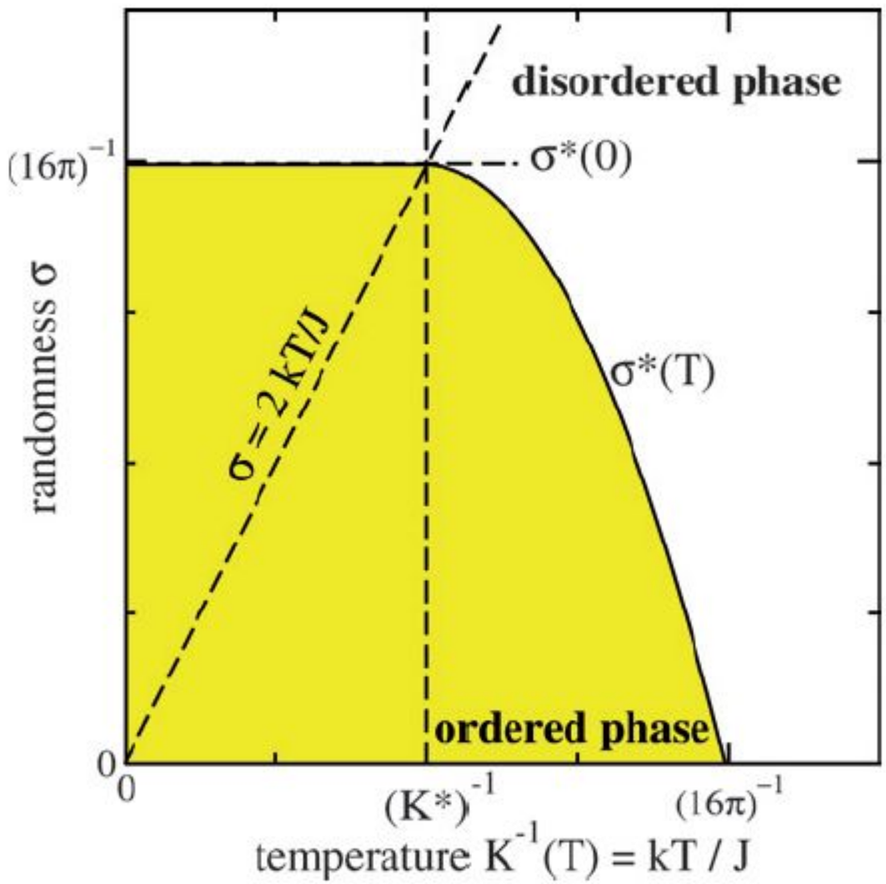
$$\Delta F = \int \left(\frac{1}{2} K_A (f_6^0)^2 (\nabla \phi)^2 + a_6(T - T_c)(f_6^0)^2 + b(f_6^0)^4 \right) d\mathbf{r}$$

Unbinding of the singular topological defects of the order-parameter phase (disclinations) at T_i - BKT transition. Continuous transition at T_i and at T_{MF}.

What is the mechanism of the first-order liquid-hexatic transition?

Theoretical background: Influence of random pinning on the phase diagram

In experim… …lsorption
on an inte… …on solid
substrates… …rder due
to some rc…



As it was… …e melting
scenario… …R. Nelson,
Phys. Rev… …, J. Phys.
C-Solid S… …nd H. A.
Fertig, Pl… …range of
the hexa… …hile T_i is
predicted… …ases with
increasin… …e can be
establish…