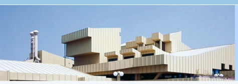


Phase transitions in two-dimensional colloidal systems

Zakopane, 21.5.2013

Peter Keim
Universität Konstanz

Soft matter systems:

Fog, dust, emulsions, suspensions, foam, etc. (often mixtures on the micron-skale) also, milk, blood, biological tissue...

Colloidal systems: solid particles (100nm – 1μm) dispersed in a solvent.

Energy between particles ~ eV (like atoms)
Length scales 10^5-10^6 times larger than in 'classical' solid state
Energy densities → elastic moduli 10^{15}-10^{18} times smaller

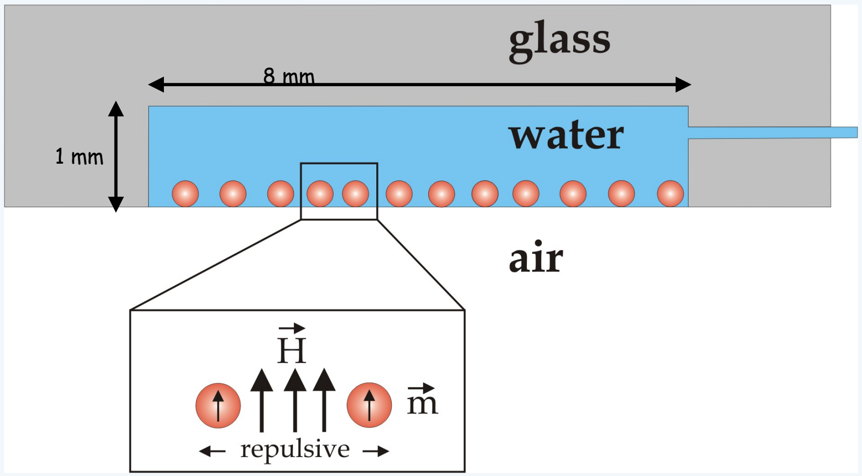
→ SOFT

Boltzmann constant k_B is important
(forget Planck's h)

Outline

- Experimental setup & video microscopy
- How crystalline is a 2D crystal?
- Dispersion-relation of a 2D lattice
- Melting in two Dimensions
- Renormalization of Young's modulus
- The hexatic phase (fluid with sixfold director)
- Summary

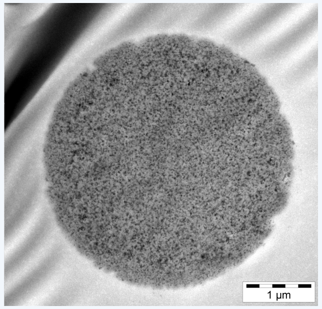
Experimenal setup



Colloid properties :

- diameter 4.5µm
- density 1.5g/cm^3
- superparamagnetic due to Fe_2O_3-doping

- hanging droplet geometry, colloids confined at water/air-interface
- magnetic field *H* perpendicular to water/air-interface
- induced dipole moments lead to repulsive interaction



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

Image processing

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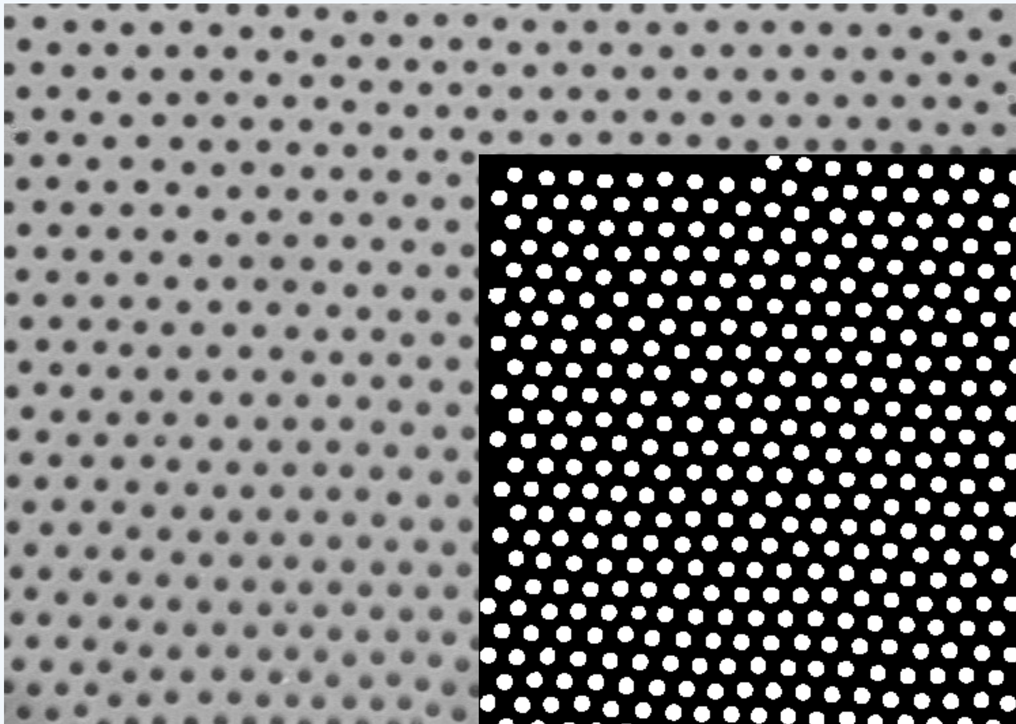
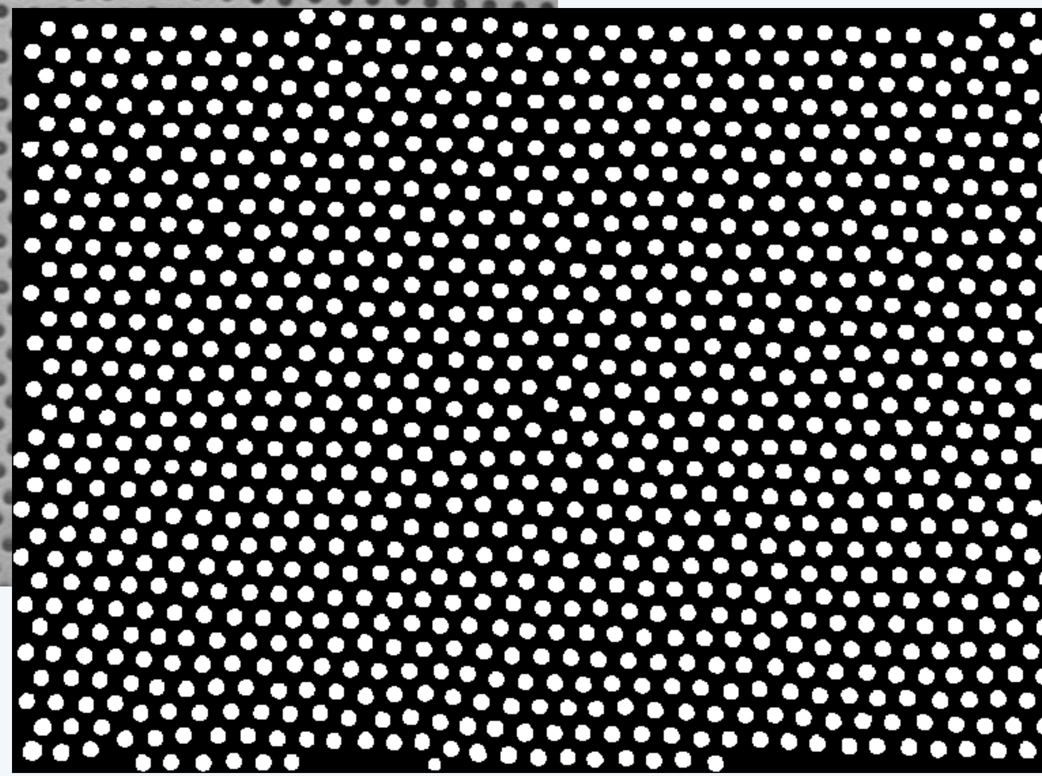


videomicroscopy

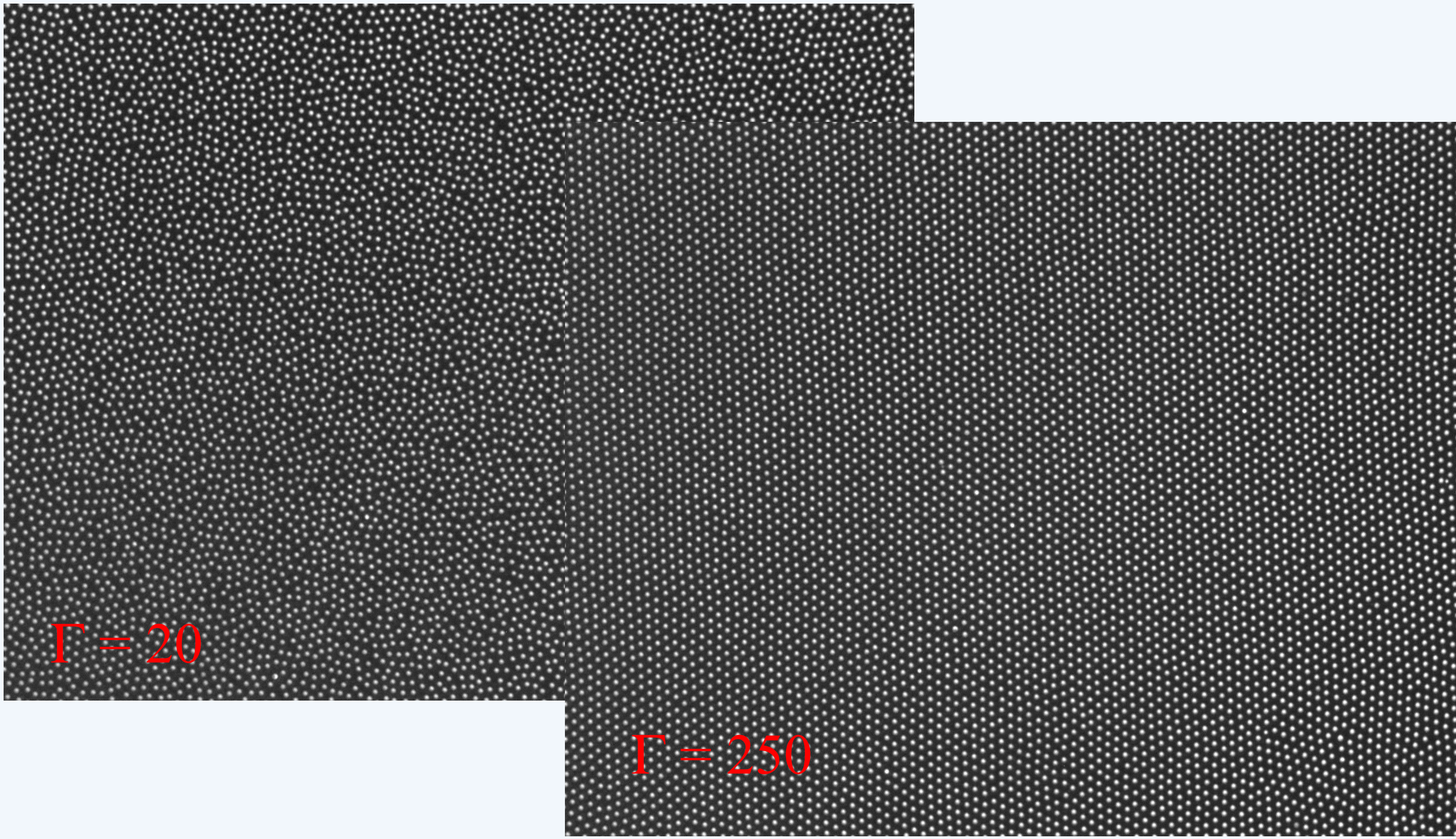


binarized image

Whole image: 830 μm *620 μm
contains 2500-3000 colloids

binarized large object (blob)-analysis

Real space image

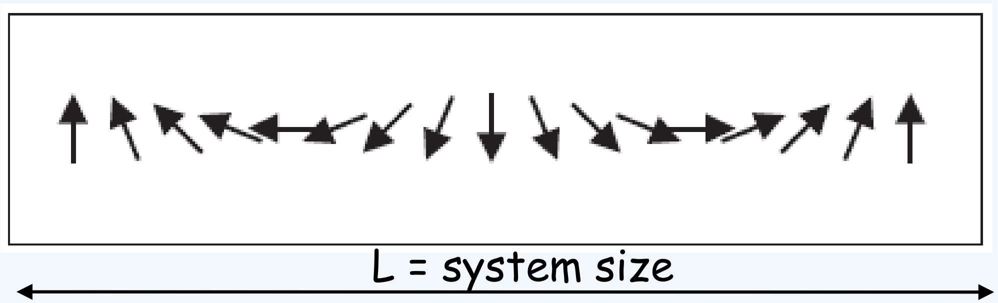


Up to 10000 particles,
field of view: 1160x850μm

$\Gamma_{melt} = 60$

Whole sample: 8 mm diameter
contains up to 300.000 colloids

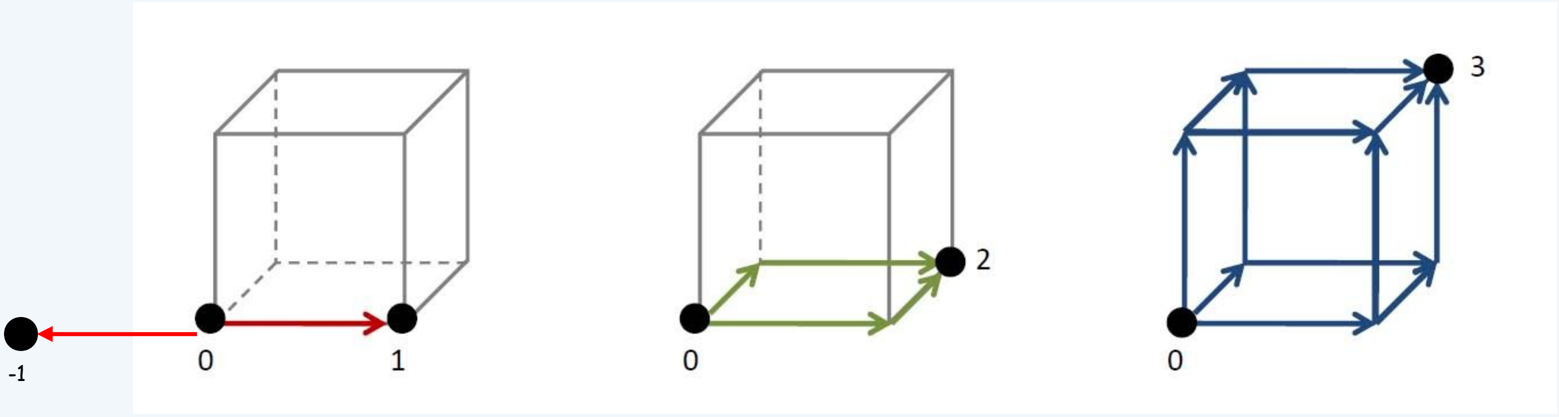
How crystalline is a 2D crystal?



$$E \propto N\phi^2 \propto L \cdot \left(\frac{2\pi}{L}\right)^2$$

$$E \propto L^2 \cdot \left(\frac{2\pi}{L}\right)^2 \quad \text{in 2D}$$

$$E \propto L^3 \cdot \left(\frac{2\pi}{L}\right)^2 \quad \text{in 3D}$$

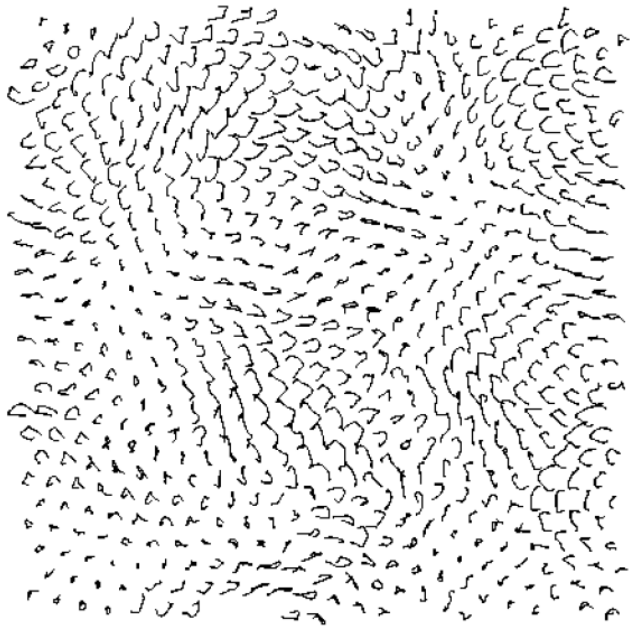


fluctuations between 0 and 1 ~ ξ
fluc. between –1 and 1 ~ \sqrt{2}* ξ <- because they add up independently !

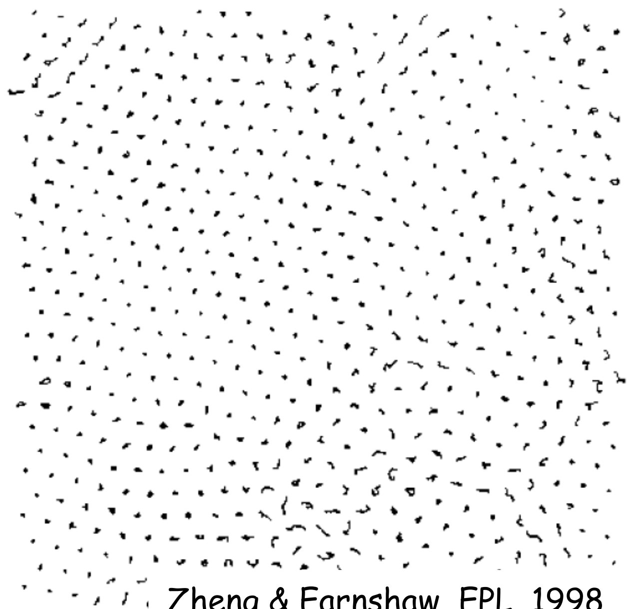
Peierls, 1935

2D Lindemann criterion

trajectories



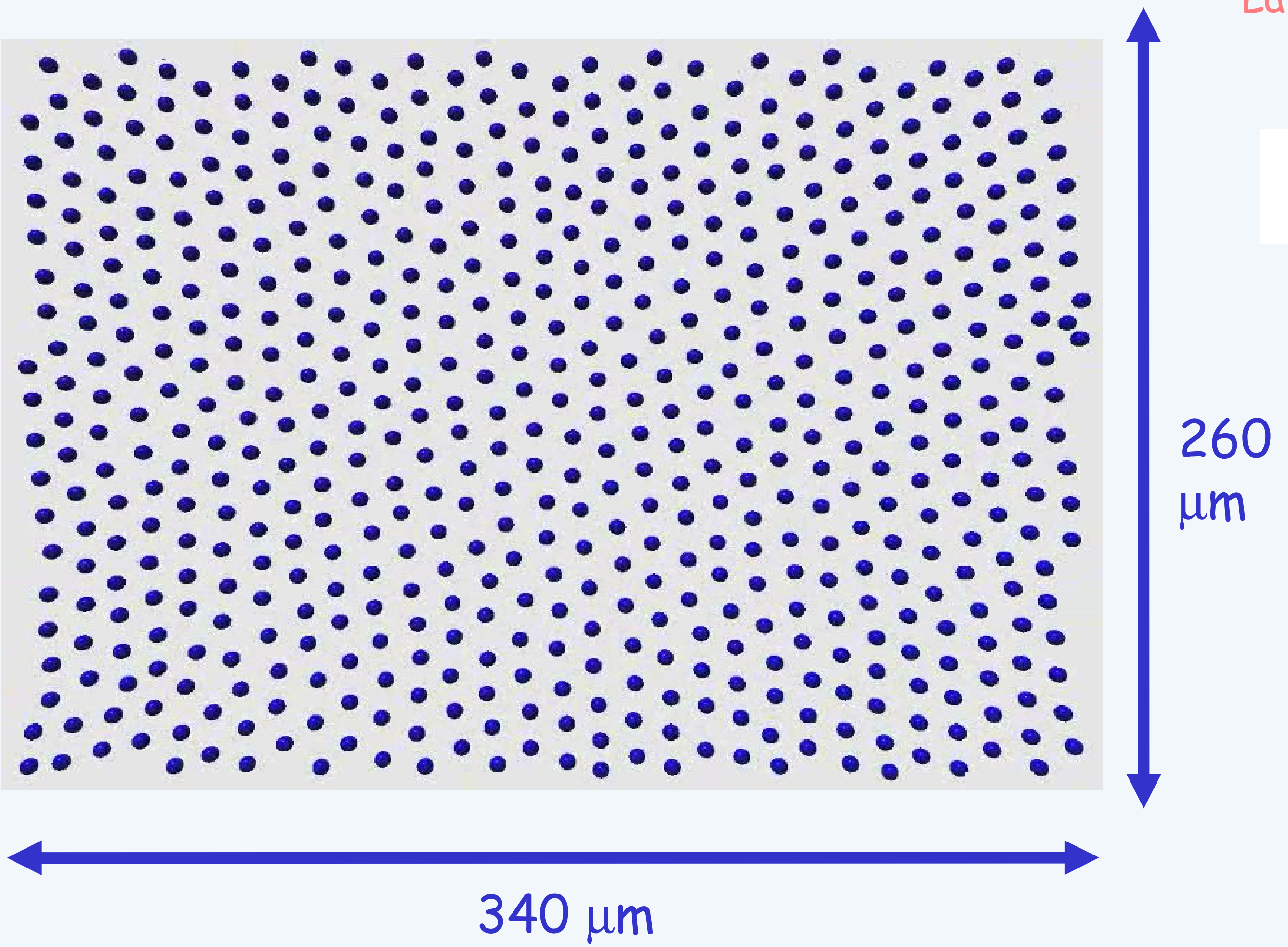
... relative to nearest neighbours



Zheng & Earnshaw, EPL, 1998

$$\gamma_L(t) = \frac{\left\langle \left[\Delta \vec{u}_j(t) - \Delta \vec{u}_{j+1}(t) \right]^2 \right\rangle}{2a^2}$$

movie



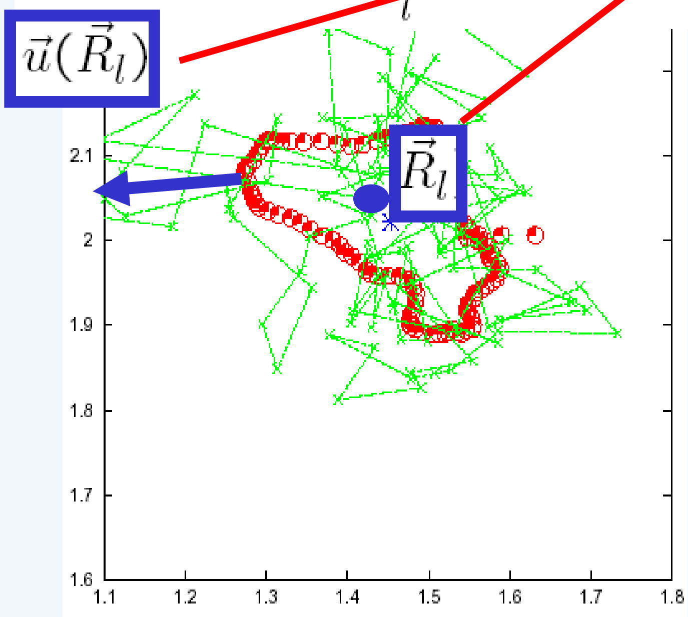
Lattice vector

$$\vec{r} \;=\; \vec{R} + \vec{u}(\vec{R})$$

Displacementvektor

local coordinates !

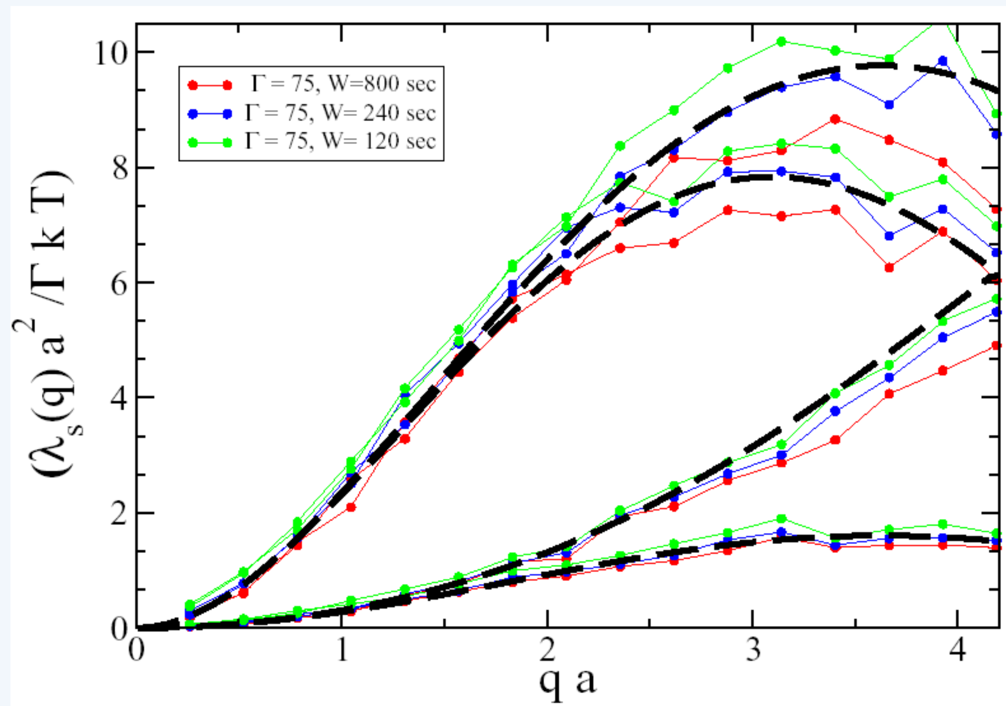
$$\vec{u}(\vec{q}) = \frac{1}{\sqrt{N}} \sum_l \vec{u}(\vec{R}_l) e^{-i\vec{q}\vec{R}_l}$$



Trajectory is averaged for a finite time-window get the equilibrium position

$\vec{u}(\vec{R}_l)$

displacement is taken relative to the averaged postion....



Equipartition theorem

.... Every mode has energy $k_B T/2$

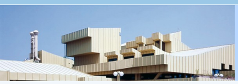
$$\frac{1}{2}\left\langle u_\mu^*(\vec{q}) D_{\mu\nu}(\vec{q}) u_\nu(\vec{q})\right\rangle = \frac{1}{2} k_B T$$

$$\langle u_\mu^*(\vec{q}) u_\nu(\vec{q})\rangle \quad = \quad kT D_{\mu,\nu}^{-1}(\vec{q})$$

$$D_{\mu\nu}(\vec{q}) \cdot \frac{a^2}{k_B T\, \Gamma} = \tilde{D}_{\mu\nu}(\vec{q})$$

$$p_s(\vec{q}) = \Gamma \left\langle u_\mu^*(\vec{q}) \cdot u_\nu(\vec{q})\right\rangle / a^2$$

$$\frac{1}{p_s(\vec{q})} = \frac{\lambda_s(\vec{q}) a^2}{k_B T\, \Gamma}$$



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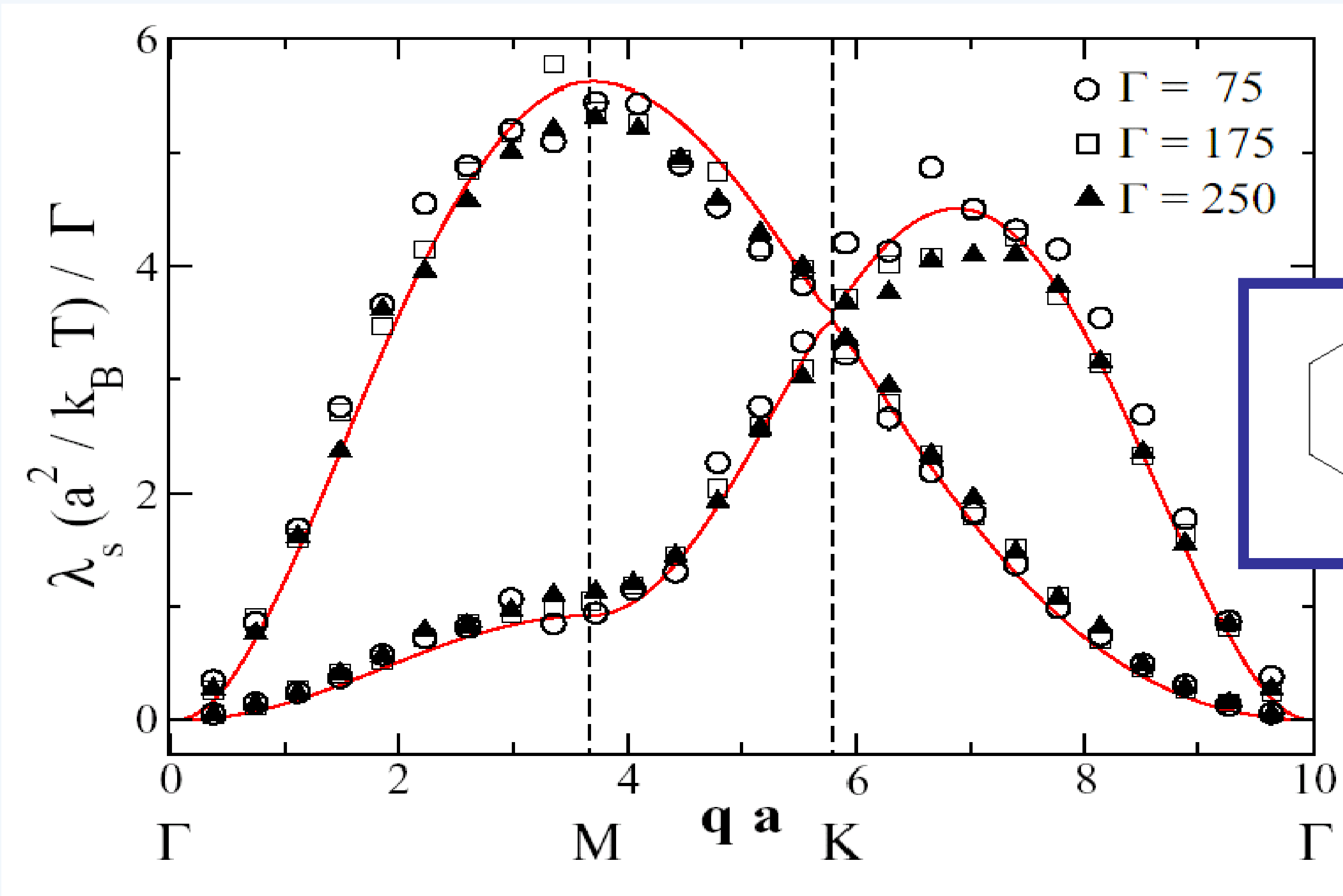
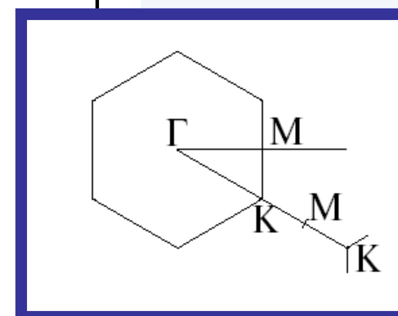
„Dispersion"-relation





PRL, **92**, 215504 (2004)

Limes q -> 0

$q \longrightarrow 0$: oscillation $\longrightarrow$ translation

lattice $\longrightarrow$ elastic continuum

spring constant $\longrightarrow$ <u>elastic moduli</u>

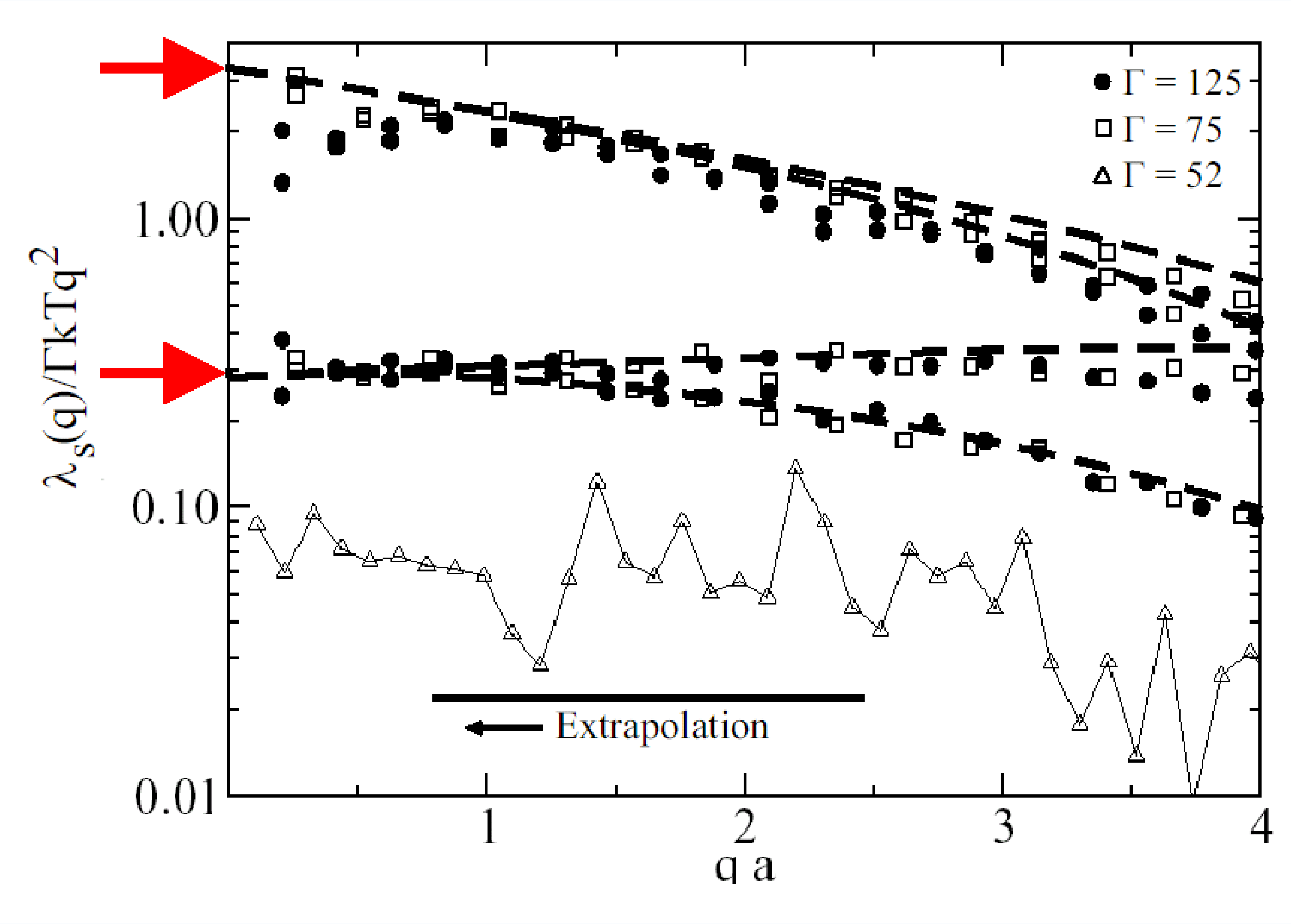
μ Shear modulus

$\lambda + \mu$ Bulk modulus in 2D

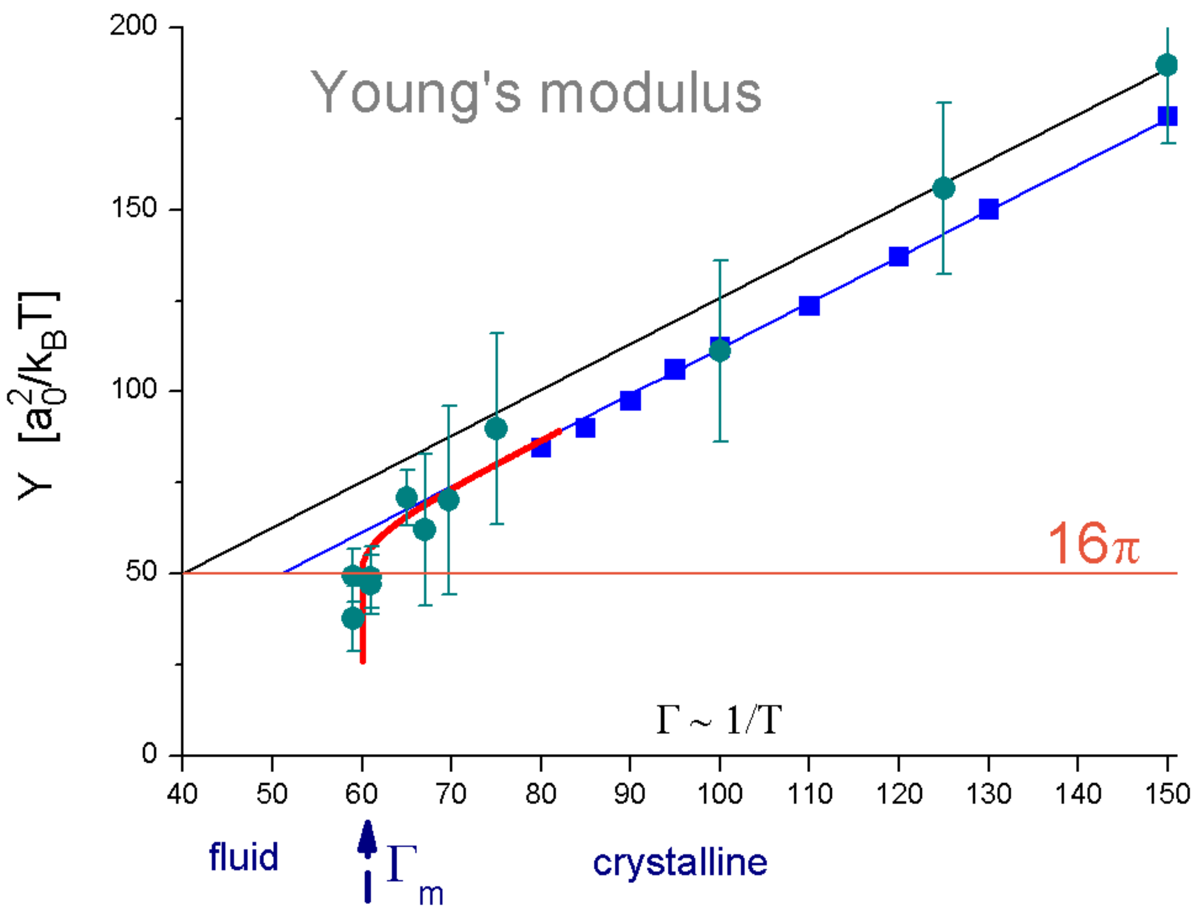
$$\frac{v_0(2\mu+\lambda)}{k_B T} = \lim_{\vec{q}\to 0} \left(q^2 \langle |u_{||}(\vec{q})|^2 \rangle\right)^{-1} = \lim_{\vec{q}\to 0} q^2/k_B T \cdot \lambda_l(\vec{q})$$

$$\frac{v_0\mu}{k_B T} = \lim_{\vec{q}\to 0} \left(q^2 \langle |u_{\perp}(\vec{q})|^2 \rangle\right)^{-1} = \lim_{\vec{q}\to 0} q^2/k_B T \cdot \lambda_t(\vec{q})$$

elastic moduli

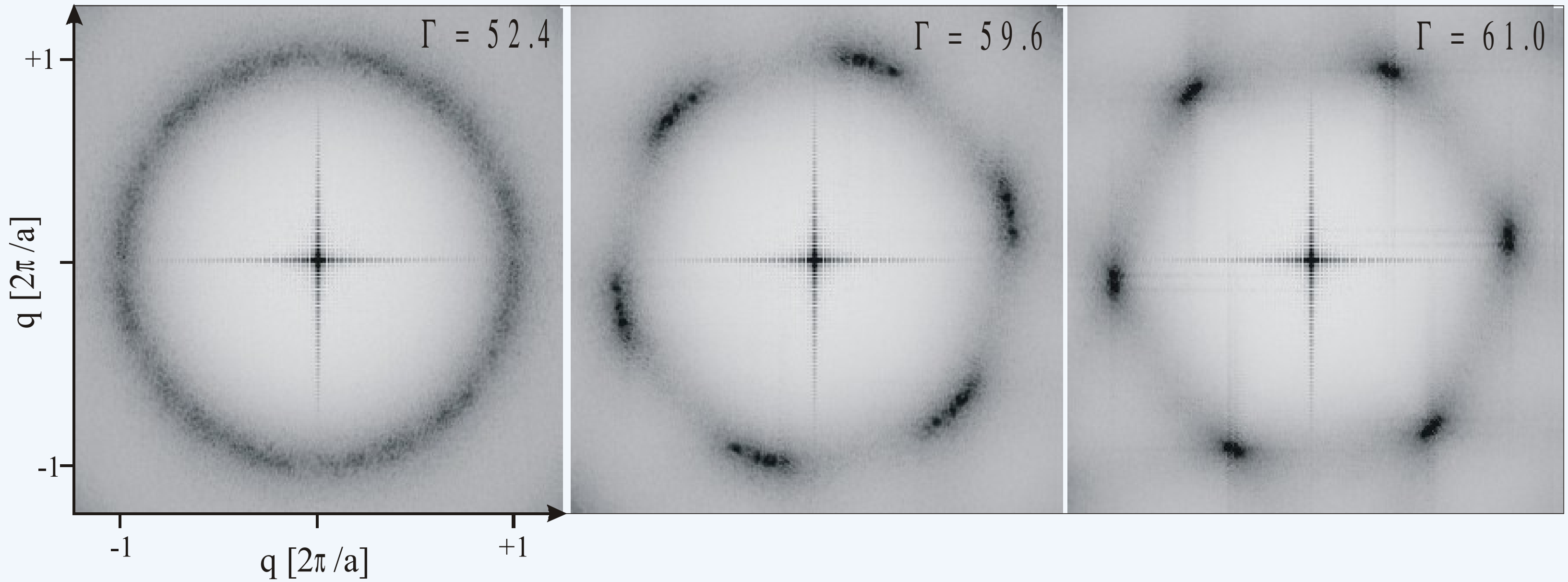


Young's modulus



PRL, **93**, 255703 (2004)

Structurefactor



$$S(\vec{q}) = \frac{1}{N}\langle \sum_{\alpha,\alpha'} e^{-i\vec{q}(\vec{r}_\alpha - \vec{r}_{\alpha'})}\rangle$$

KTHNY-Theory

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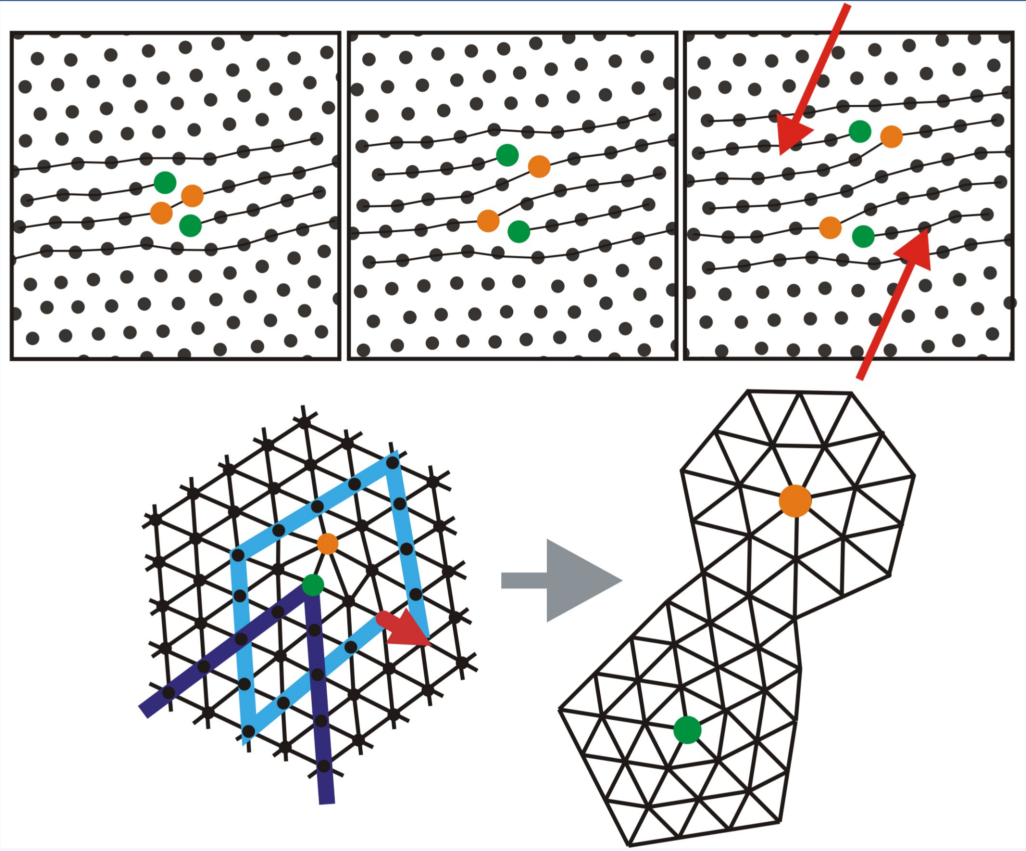
- 2d melting-theory by Kosterlitz, Thouless, Halperin, Nelson, and Young
- two transitions of continuous order
- topological defects break translational- and rotational symmetry
  - but at different temperatures.



Dislocation pairs

Disclination pairs

Defect Hamiltonian

Dislocations:

$$H_{Disl} = -\frac{a_0^2 K}{4\pi}\frac{1}{2}\sum_{\alpha\neq\alpha'}[\vec{b}(\vec{r}_\alpha)\cdot\vec{b}(\vec{r}_{\alpha'})\ln\frac{R_{\alpha,\alpha'}}{a} - \frac{[\vec{b}(\vec{r}_\alpha)\cdot\vec{R}_{\alpha,\alpha'}]\,[\vec{b}(\vec{r}_{\alpha'})\cdot\vec{R}_{\alpha,\alpha'}]}{R^2_{\alpha,\alpha'}}]$$

$$+ \; E_c\sum_\alpha|\vec{b}(\vec{r}_\alpha)|^2 \quad \text{with} \quad K = \frac{4\mu(\mu+\lambda)}{2\mu+\lambda} \quad \text{Young's modulus}$$

Disclinations:

$$H_{Disc} = -\frac{F_A}{2\pi}\left(\frac{\pi}{3}\right)^2\frac{1}{2}\sum_{\alpha\neq\alpha'} s_\alpha s_{\alpha'}\ln\frac{R_{\alpha,\alpha'}}{a_s} + E_s\sum_\alpha s_\alpha^2 \quad \text{with}$$

$$F_A = \text{Frank's modulus}$$

pair-potential of defects for large distances:

$$\beta v(r) = c_D \ln\frac{r}{a_D}$$

$$c_{Disl} = \frac{\beta K a_0^2}{4\pi}$$ for dislocation pairs

$$c_{Disc} = \frac{\beta F_A \pi}{18}$$ for disclination pairs

PRL **95**, 185502 (2005)

Defect unbinding

average distance between defect pairs:

$$\langle r^2 \rangle = \frac{\int d^2r \, r^2 e^{-\beta v(r)}}{\int d^2r \, e^{-\beta v(r)}} = \frac{2 - c_D}{4 - c_D} \, a^2 \qquad \langle r^2 \rangle \to \infty \text{ for } c_D = 4$$

unbinding of dislocation pairs:

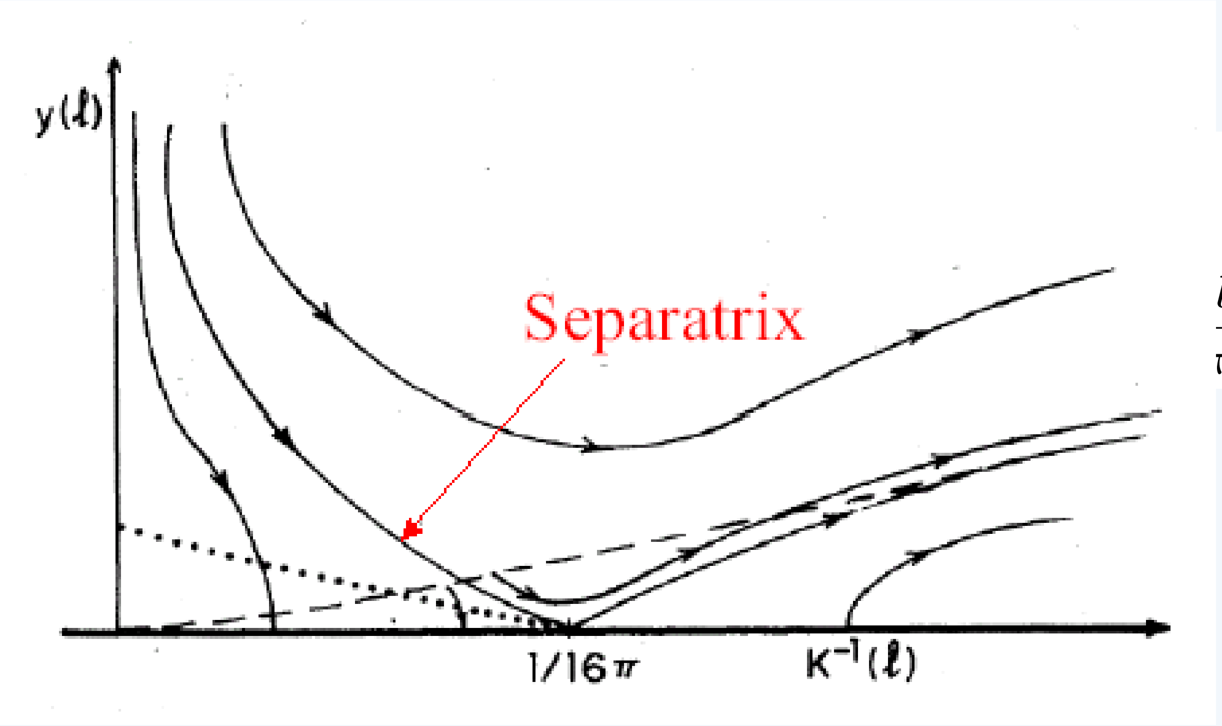
$$\frac{\beta K a_0^2}{4\pi} \to 4 \quad \Rightarrow \quad \lim_{T \to T_m} \frac{K a_0^2}{k_B T} = 16\pi$$

unbinding of disclination pairs:

$$\frac{\beta F_A \pi}{18} \to 4 \quad \Rightarrow \quad \lim_{T \to T_i} \frac{F_A}{k_B T} = 72/\pi$$

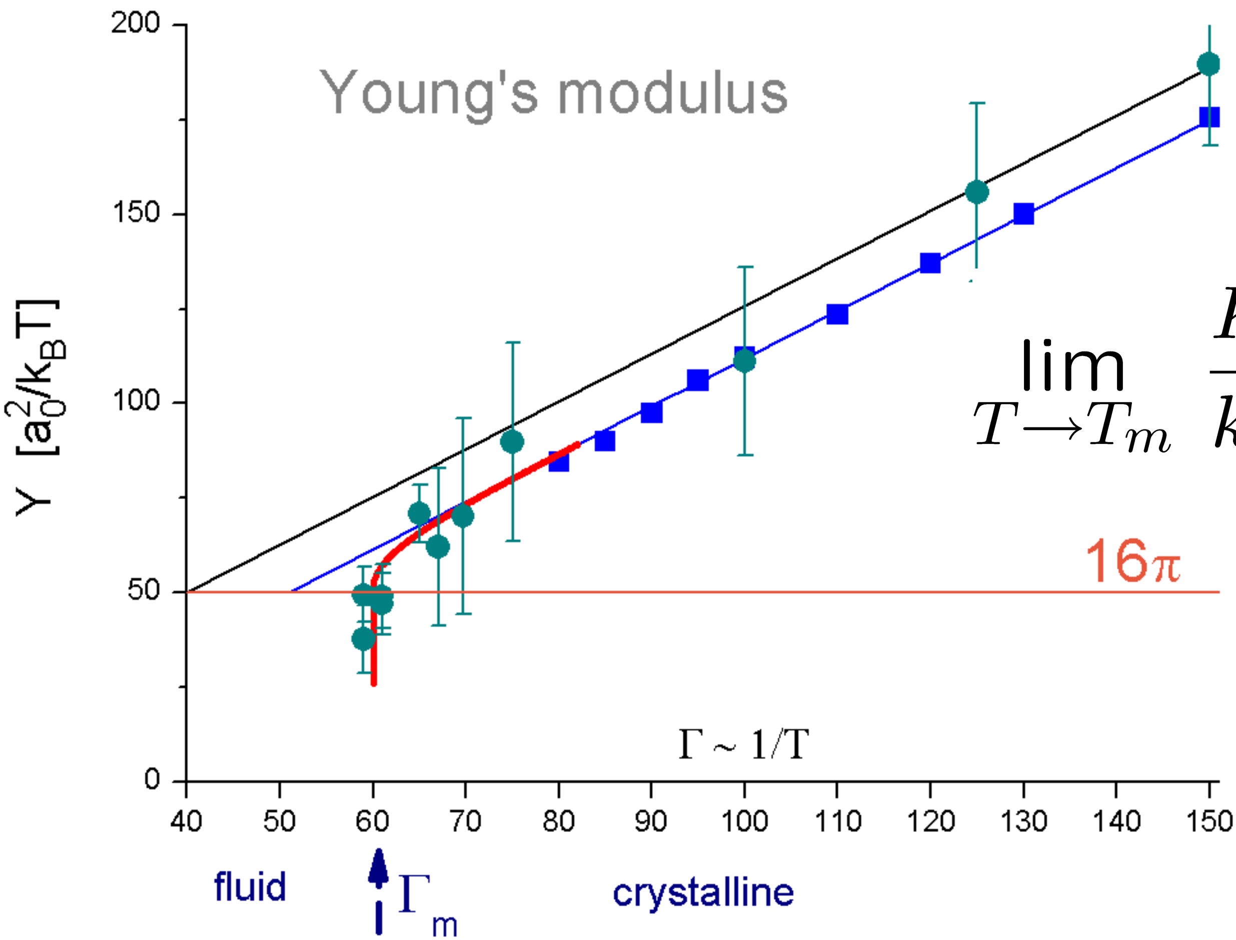
Renormalization

Youngs modulus depends on the probability: $y = \exp(-E_C/k_B T)$
of the creation of a dislocation wich itself depends on Youngs modulus.
Renormalization group theory leads to recursion relations:



$$K = \frac{4a_0^2}{k_B T}\frac{4\mu(\mu+\lambda)}{2\mu+\lambda}$$

Young's modulus



$$\lim_{T \to T_m} \frac{K a_0^2}{k_B T} = 16\pi$$

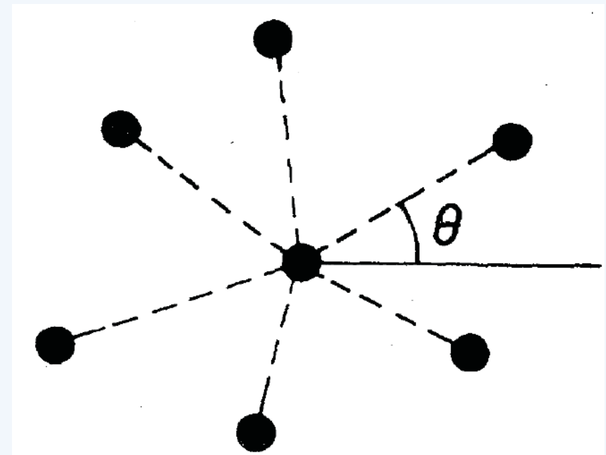
PRL. **93**, 255703 (2004)

Orientational order

„Bond order“ correlation function

$$G_6(r) = \langle \psi(\vec{r})\psi^*(\vec{0}) \rangle$$

$$\psi_i(\vec{r}) = \frac{1}{N_j}\sum_j e^{6i\theta_{ij}(\vec{r})}$$



crystalline: $T<T_m$	$\lim_{r\to\infty} G_6(r) \neq 0$	long range order
hexatic: $T_m<T<T_i$	$G_6(r) \sim r^{-\eta_6}$	quasi long range
isotropic: $T>T_i$	$G_6(r) \sim e^{-r/\xi_6}$	short range

Orientational correlation function

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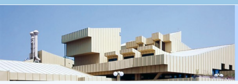
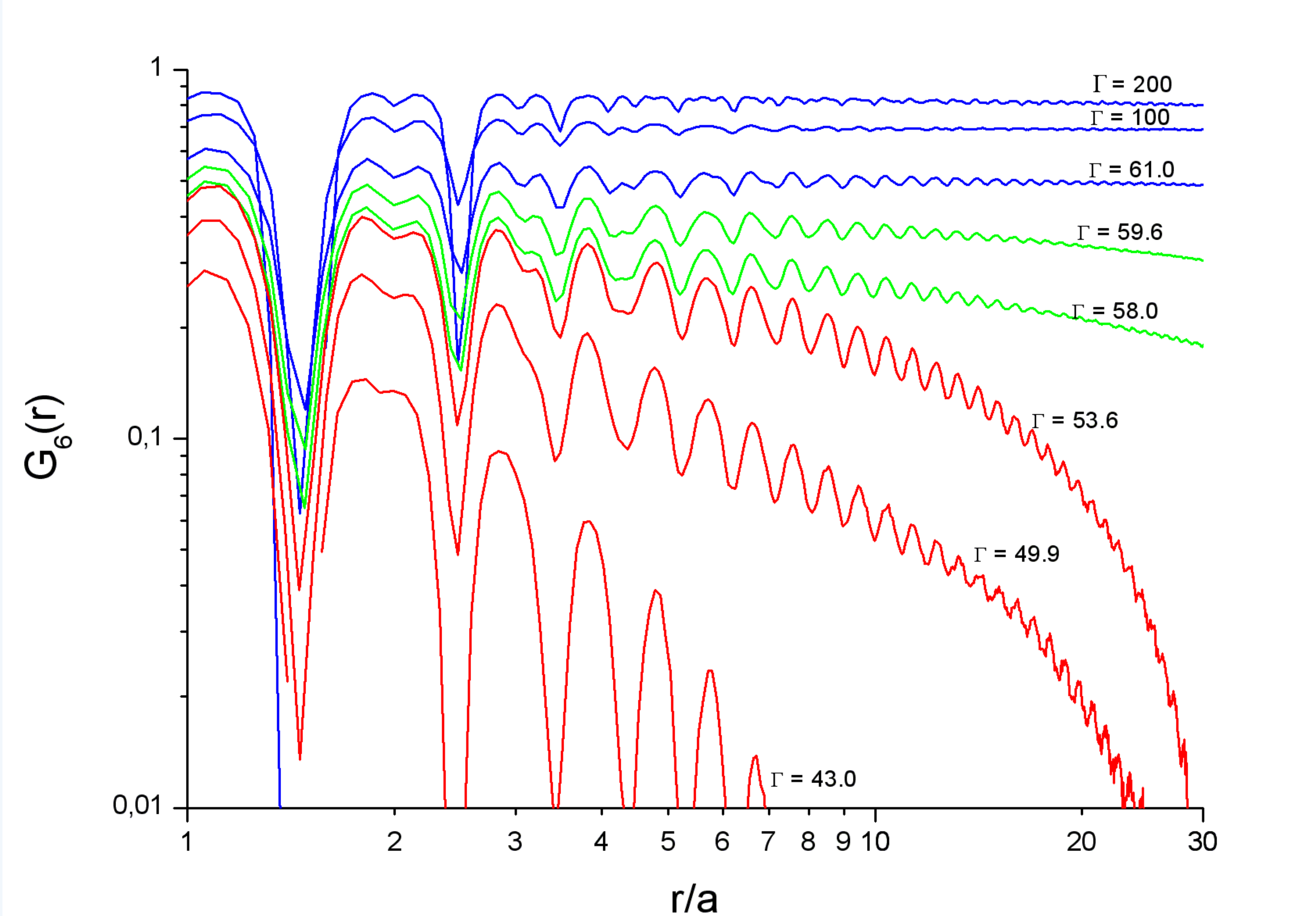


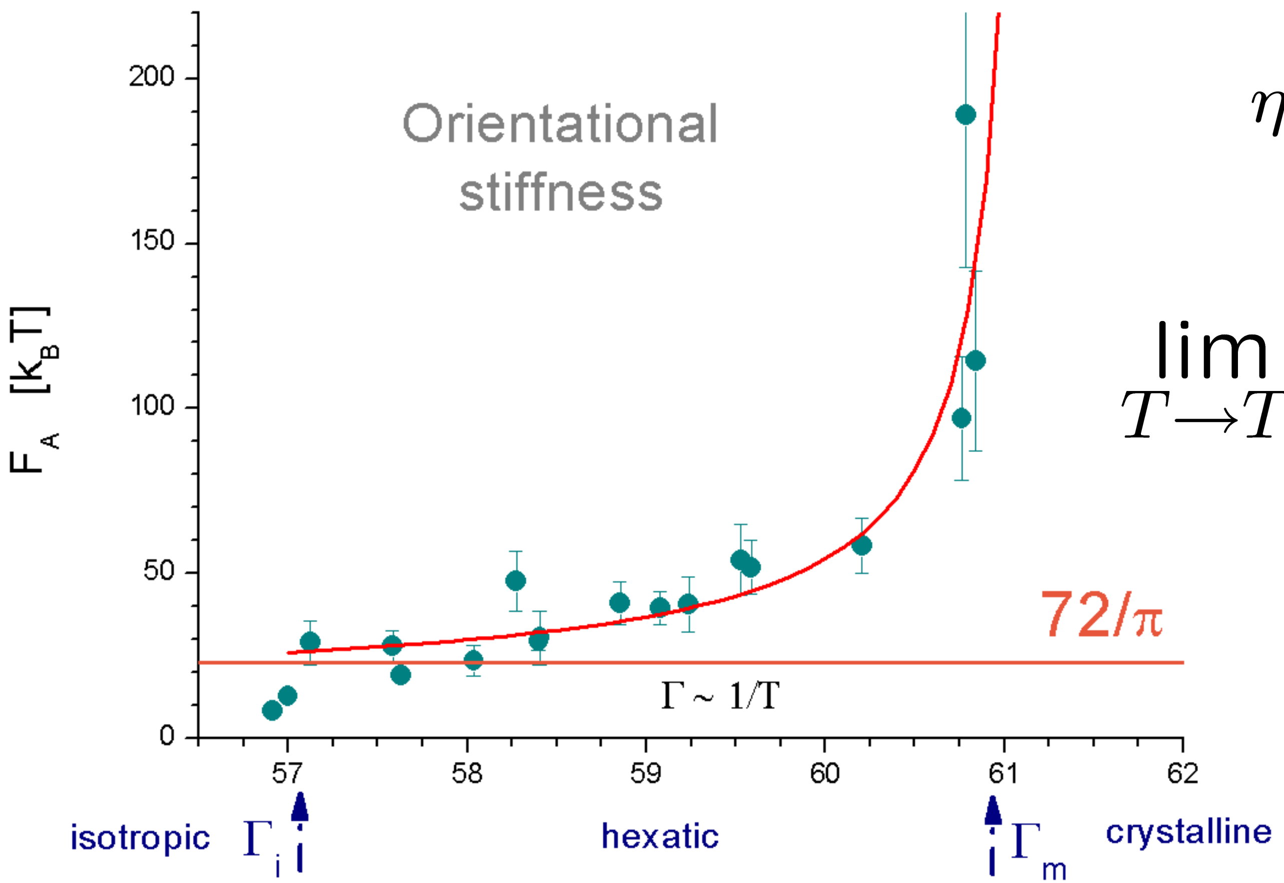


liquid <-> hexatic: $\Gamma_i = 57.5$

hexatic <-> crystal: $\Gamma_m = 60.5$

PRE, **75**, 031402 (2007)

Frank's constant

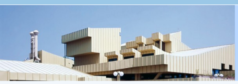


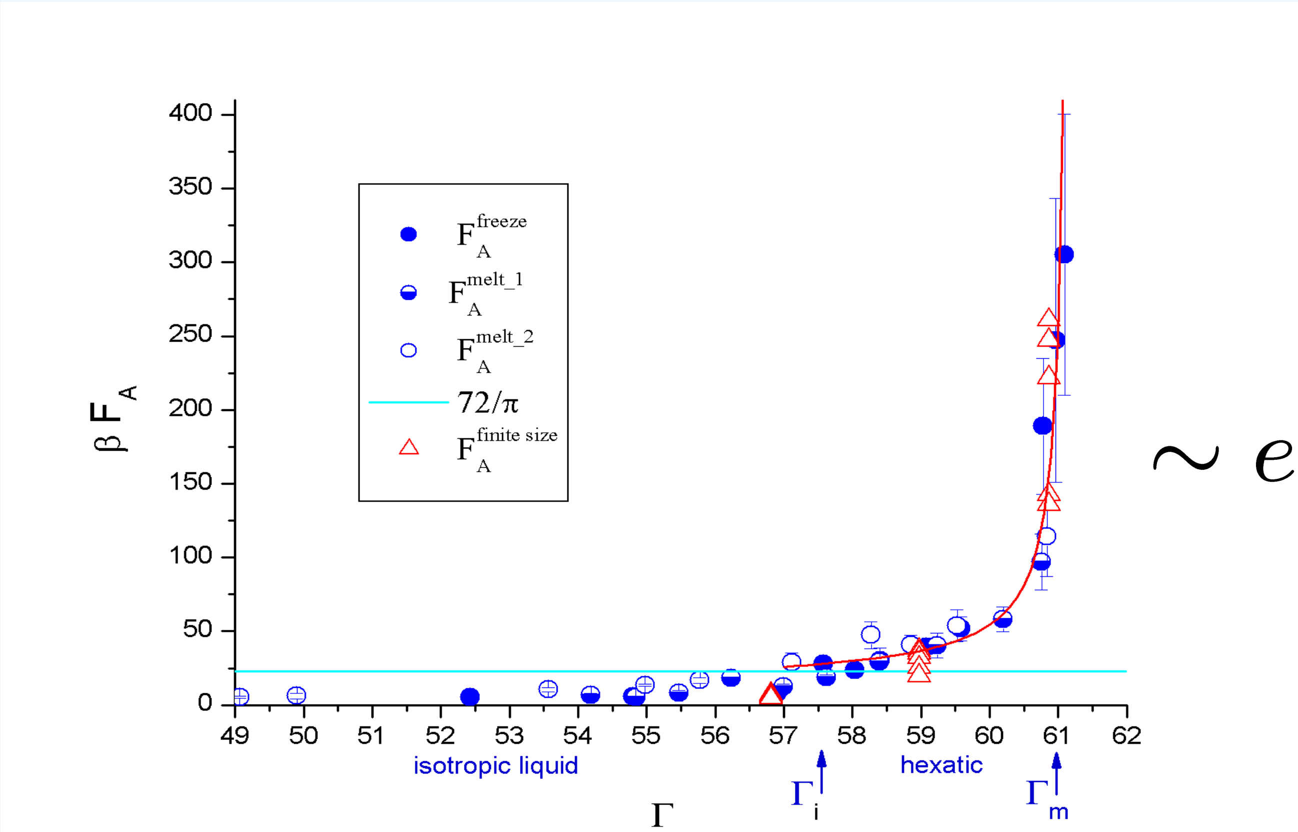
$$\eta_6(\Gamma) = \frac{18 k_B T}{\pi F_A(\Gamma)}$$

$$\lim_{T \to T_i} \frac{F_A}{k_B T} = 72/\pi$$

F_A drops below $72/\pi$ at $\Gamma_i = 57.5$

Divergence of F_A at Γ_m





$$F_A(\Gamma) \sim \xi_+^2$$

$$\sim e^{\frac{2c}{|1/\Gamma - 1/\Gamma_m|^{\bar{\nu}}}}$$

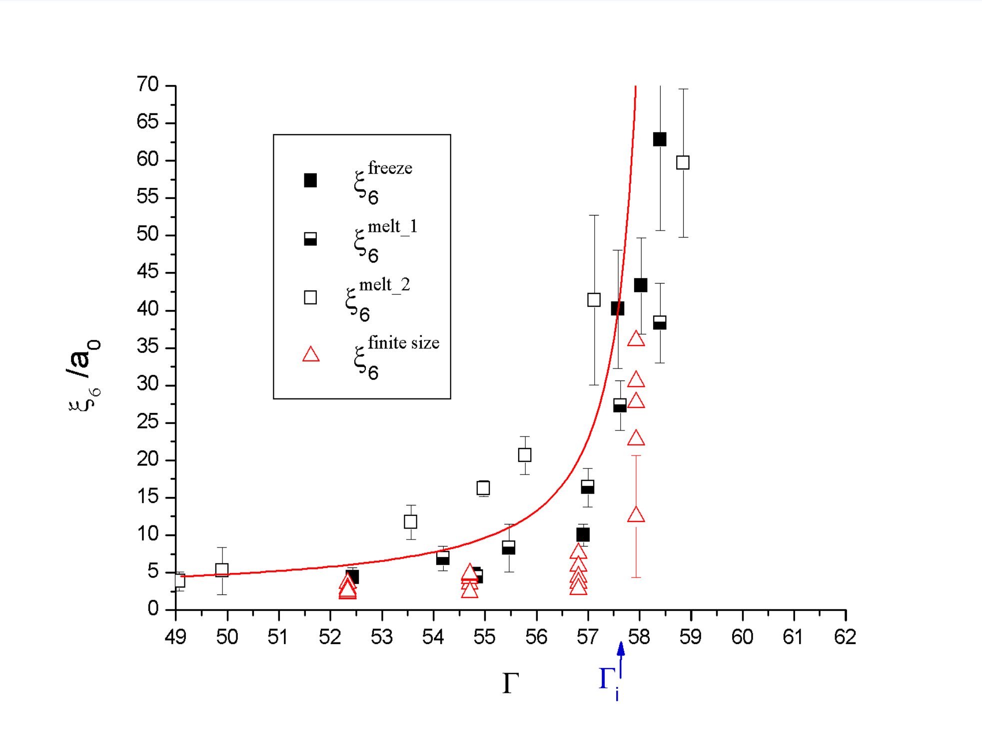
with ν = 0.36963 (Theory)

Experiment: ν = 0.35 ± 0.02

For both, melting AND freezing!

Divergence of ξ_6 at Γ_i

orientational correlation length $\xi_6(\Gamma)$:



$$\xi_6(\Gamma) \sim e^{\frac{b}{|1/\Gamma - 1/\Gamma_i|^{\nu}}}$$

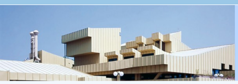
with $\nu = 0.5$

Experiment: $\nu = 0.5 \pm 0.03$

$\Gamma_i = 58.9$ → finite size effect

(of the field of view, NOT of the system)

Conclusion



- one can do 'hard' statistical physics with soft matter
- experimental realization of a 2d ensemble with tunable system temperature
- 2D Mermin-Wagner fluctuations
- „dispersion"-relation in an overdamped crystal
- Young's modulus becomes 16π at Γ_m
- Frank's constant becomes $72/\pi$ at Γ_i
- critical exponents in agreement with KTHNY-theory
- transitions are continuous, no hysteresis, no phase equilibrium