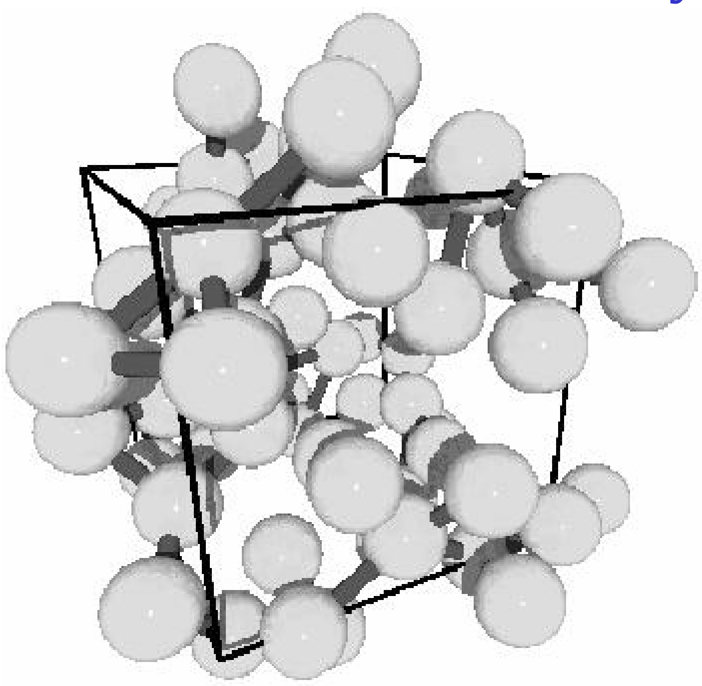
Fluctuations, Geometry and Entropic Elasticity

Yacov Kantor

Tel Aviv University



with:

Oded Farago, BGU

Michael Murat, SNRC

M. Kardar, R. Metzler,

I. Webman, T.A. Witten

Supported by | b | s | f |

FII-08, KITP, 9/2008

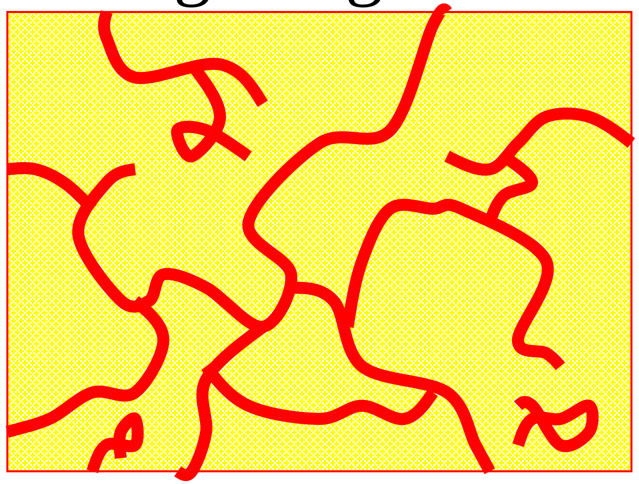
Outline

- Entropy-dominated systems - examples
- Percolating systems - conductivity vs. elasticity
- Elasticity: energy vs. entropy
- New method for calculating elastic constants
- Entropic elasticity of 2D and 3D percolating systems
- Hard ellipse solid – order and elasticity
- Conclusions

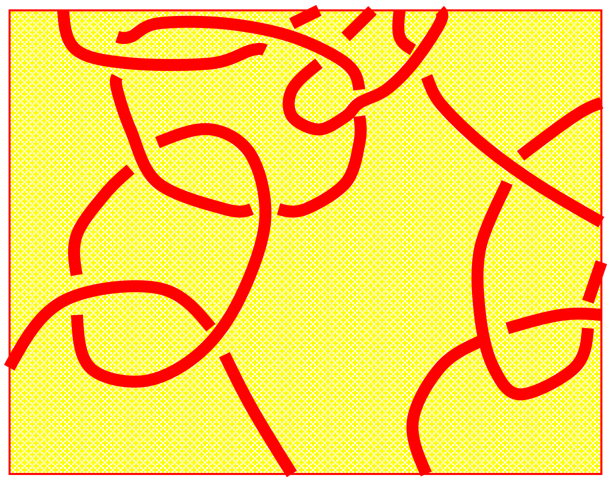
Systems with Entropic Elasticity

P.G. de Gennes, *Scaling Concepts in Polymer Physics* (1979)

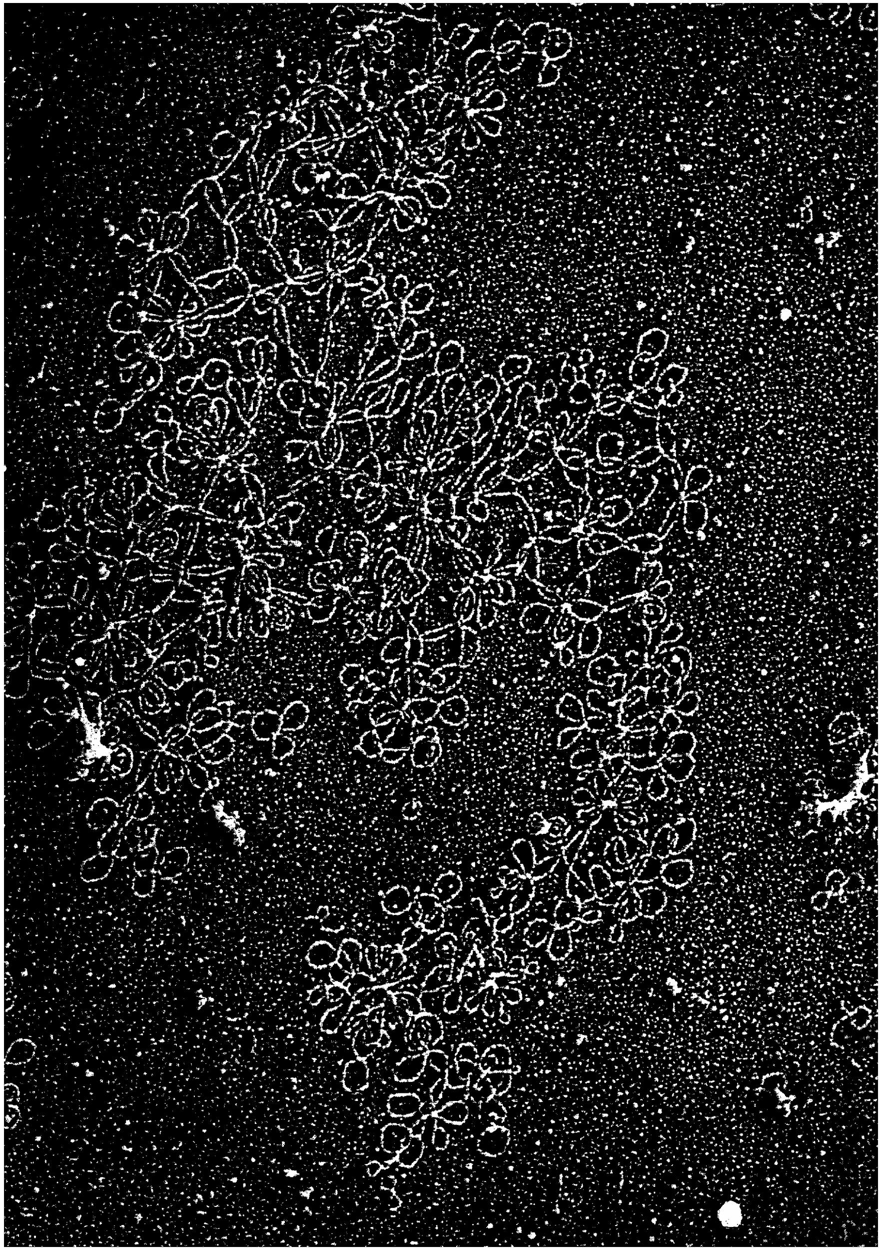
Regular gel



Olympic gel



Entanglements in DNA



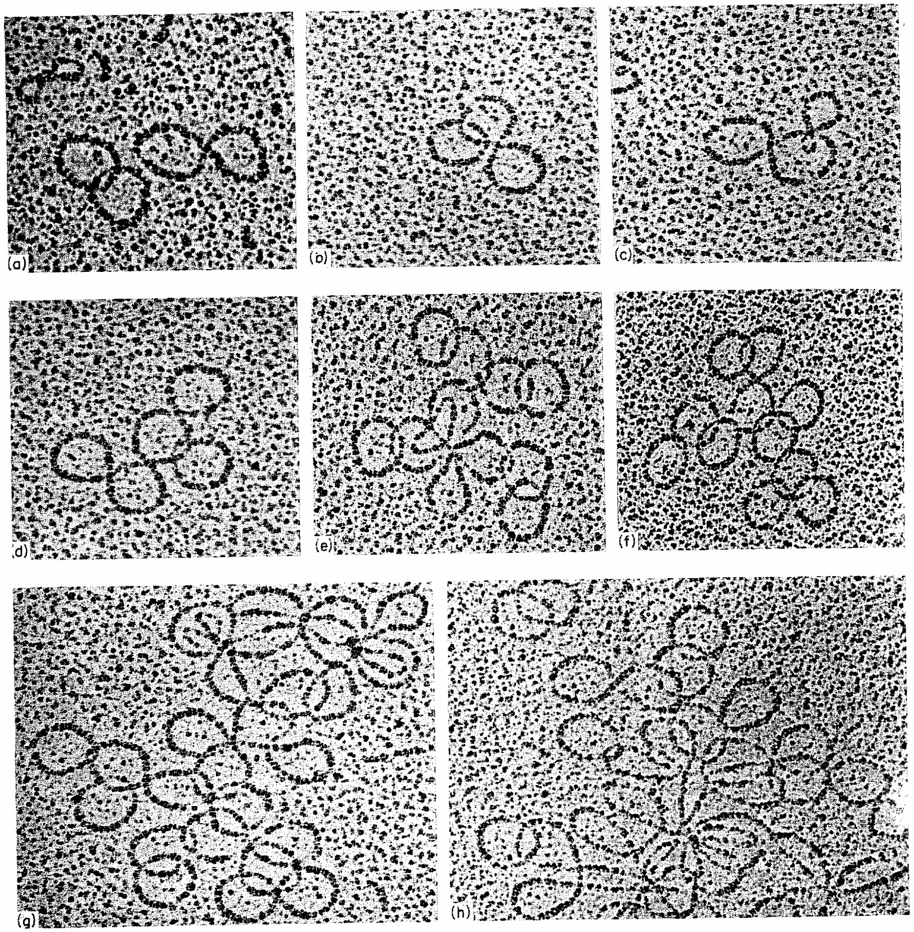


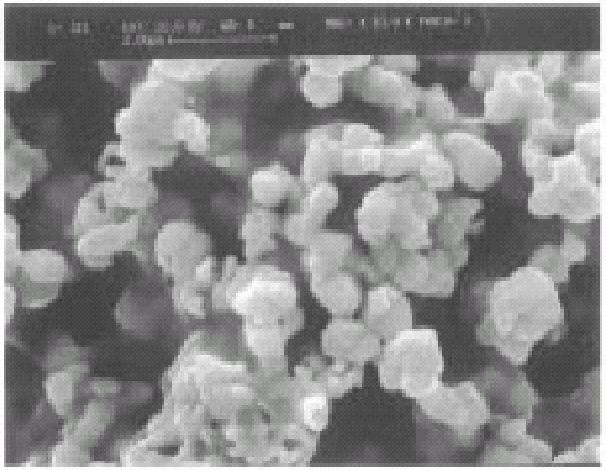
PLATE II. Electron micrographs of different molecular configurations seen in K-DNA. The contour length of a minicircle or one loop of a figure 8 is equal to 0·29 μ.

K-DNA (catenated network of DNA) is located in *kinetoplast* = organelle at the base of flagelum

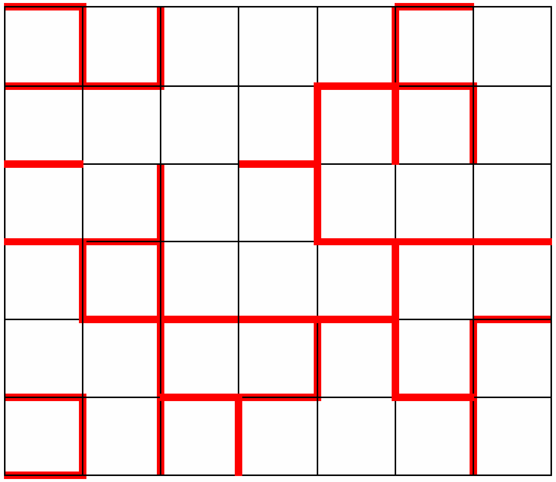
L.Simpson, A. da Silva
J.Mol.Biol. **56**, 443 (1971)

Random (percolating) system

porous ceramics

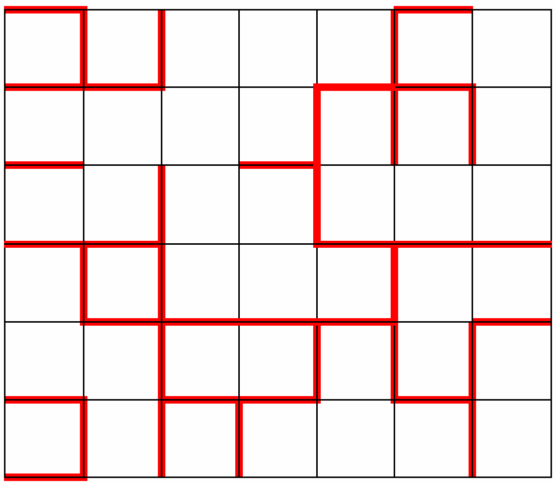


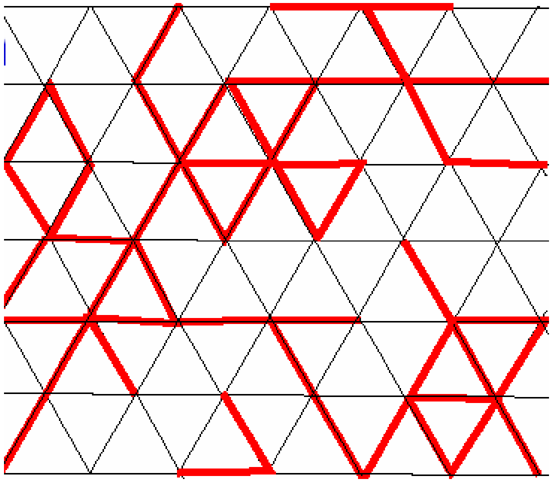
F.Craciun,C.Galassi,E.Roncari
Europhys.Lett. **41**, 55 (1998)

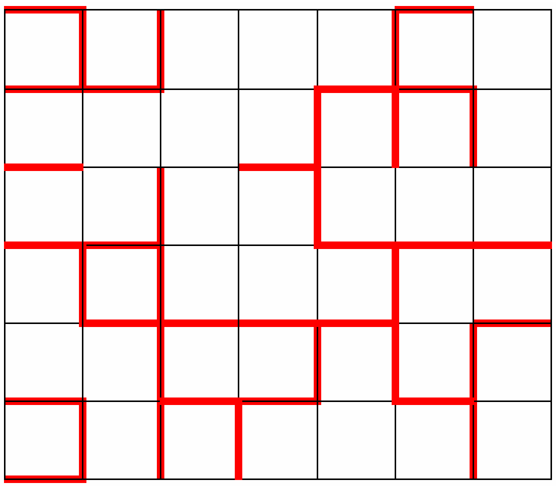


$$\kappa, \mu \sim (p - p_c)^{\tau}$$

Percolating systems







Conductivity of percolating system

$\sigma \sim (p - p_c)^t \qquad t = 1.3,\ 1.9$

$I = \sigma V \qquad$ 2D 3D

$\sum I = 0$

Rigidity percolation

$p_r > p_c$

Thorpe, J.Non Cryst.Mat.**57** (1983)
Feng,Sen PRL **52** (1984)
Jacobs,Thorpe PRL **75** (1995)

Bending elasticity

$\kappa, \mu \sim (p - p_c)^\tau \qquad \tau = 3.6,\ 3.8$

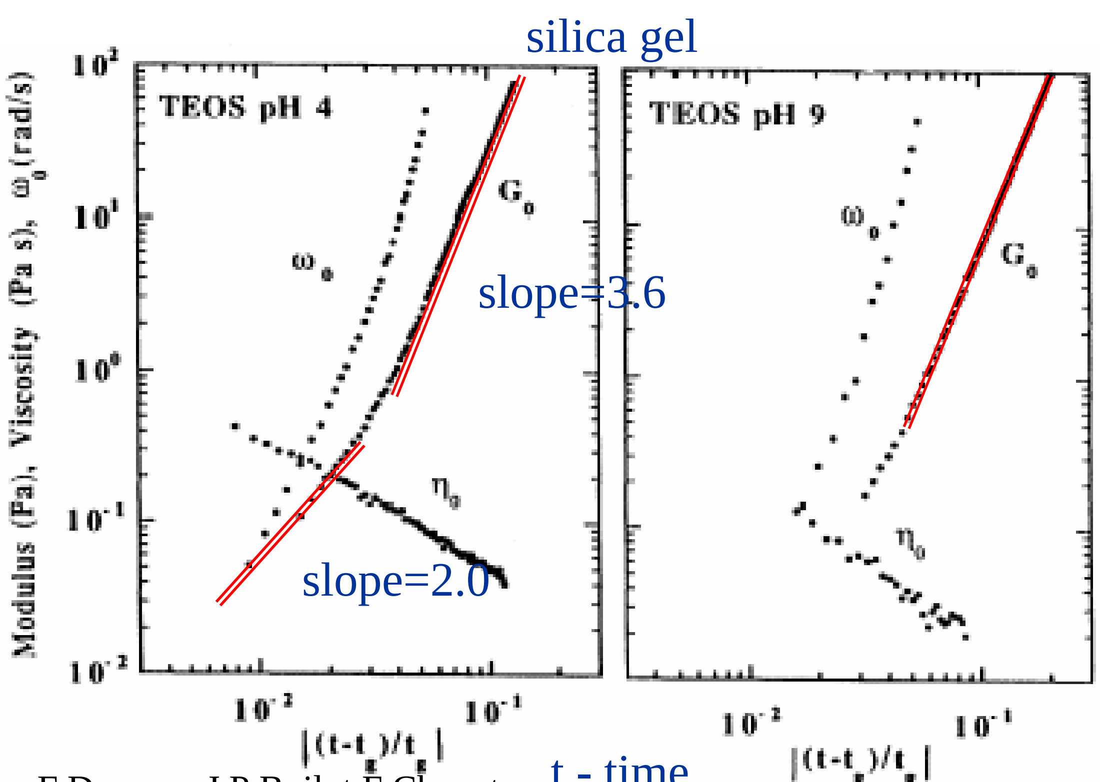
$\tau > t \qquad$ 2D 3D

force law + $\sum \vec{F} = 0$

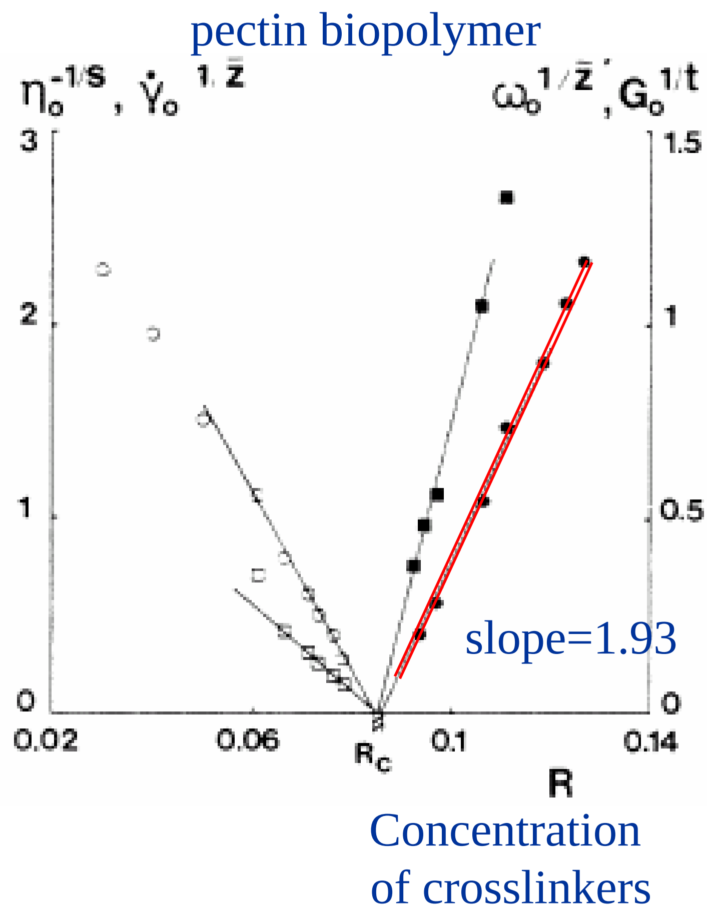
Kantor,Webman
PRL **52** (1984)

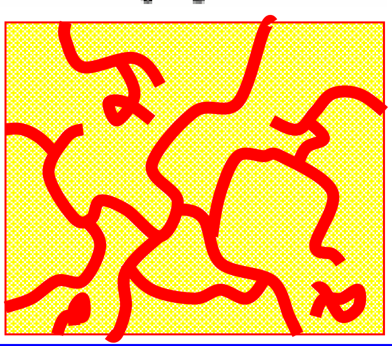
Critical index of elasticity – experimental determination

G shear modulus



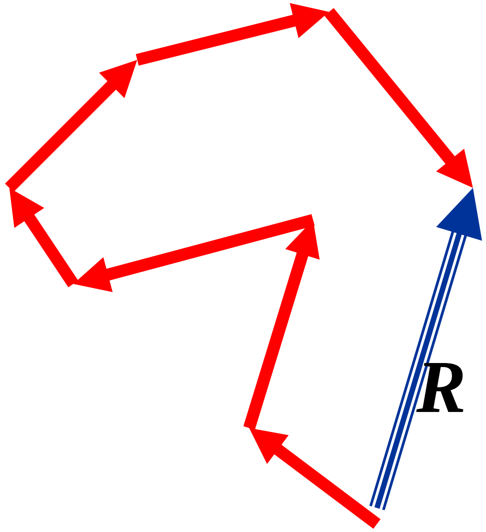
F.Devreux,J.P.Boilot,F.Chaput, L.Malier,M.A.V.Axelos
Phys.Rev.E **47**, 2689 (1993)

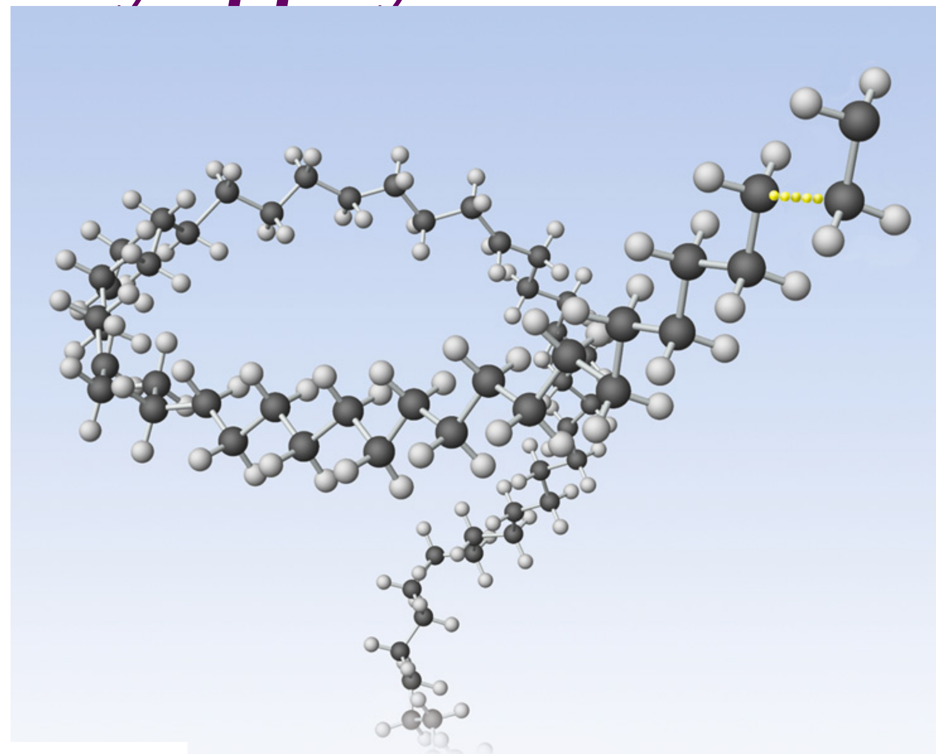




M.A.V.Axelos, M.Kolb
Phys.Rev.Lett. **64**, 1457 (1990)

Entropic elasticity of polymers



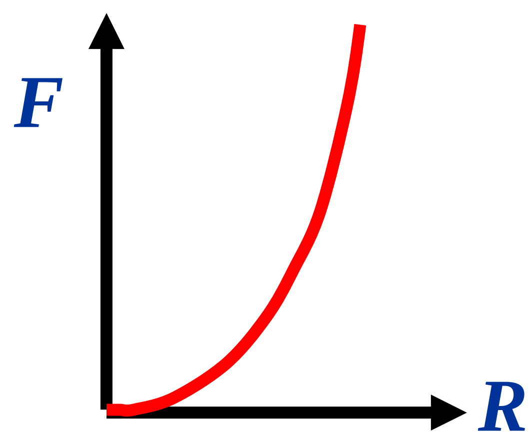


$$\vec{R} = \sum_{1}^{N} \vec{b}_i$$

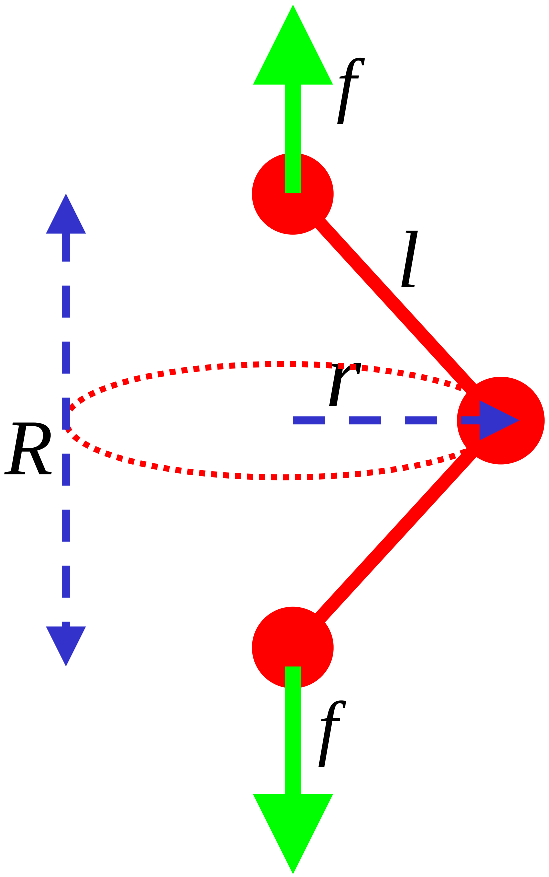
$$Z_N(R) \sim P(\vec{R}) \Rightarrow \left(\frac{3}{2\pi N \langle b^2 \rangle} \right)^{3/2} \exp\left[-\frac{3R^2}{2N\langle b^2 \rangle} \right]$$

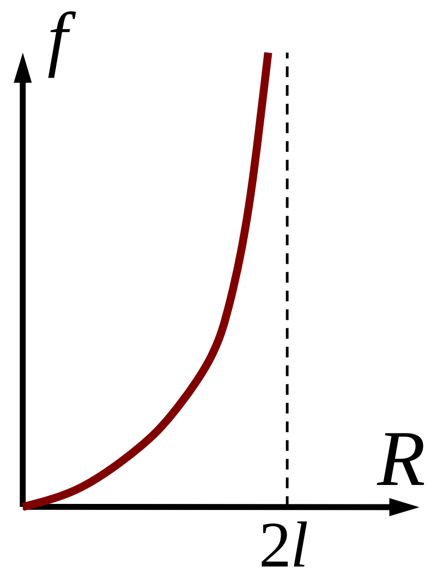
$$F(R) = -kT \ln Z(R) = \tfrac{1}{2} K R^2$$

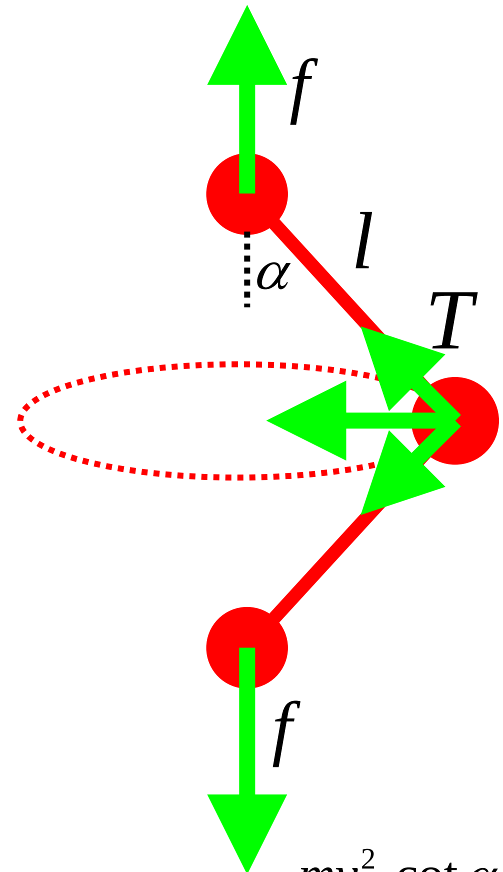
$$F(R) = \cancel{U} - TS(R)$$



Entropy and forces in "inertial regulator"







$$F = U - k_B T \ln(2\pi r) =$$

$$= \ldots - k_B T \ln 2\pi \sqrt{l^2 - \left(\frac{R}{2}\right)^2}$$

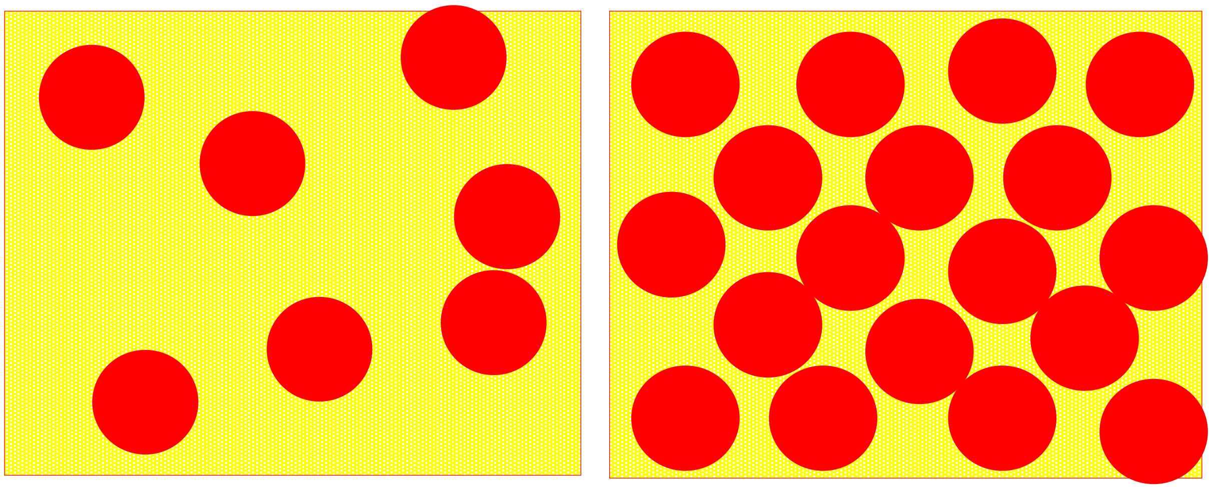
$$f = \frac{dF}{dR} = \frac{k_B T R}{4l^2 - R^2}$$

$$f = T\cos\alpha = \frac{mv^2}{r}\,\frac{\cot\alpha}{2}$$

$$\langle f \rangle = \frac{k_B T}{r}\,\frac{R}{4r}$$

Systems with Entropic Elasticity

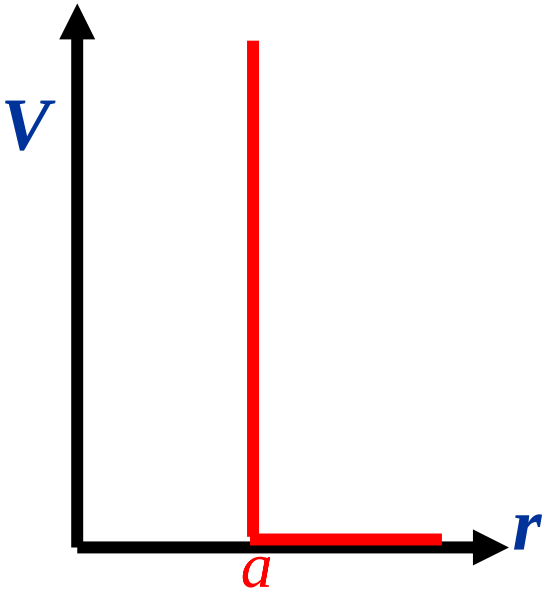
Hard sphere (or hard disk) liquid/hexatic/solid



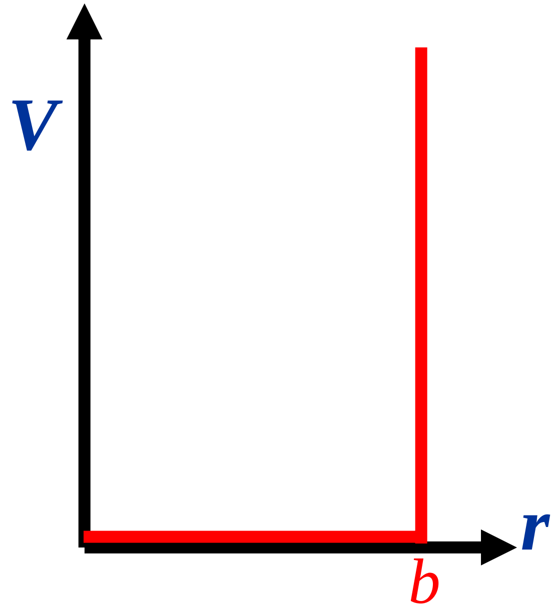
Metropolis et al. JCP **21** (53)
Alder,Wainwright JCP **27** (57)
Pusey,Magen Nature **320** (86)
Mitus et al. PRE **55** (97)
Jaster EPL **42** (98)

P. W. Bridgman, Phys. Rev. **3**, 153 (1914).
J. G. Kirkwood, J. Chem. Phys. **7**, 919 (1939).
J. G. Kirkwood, E. K. Maun and B. J. Alder, J. Chem. Phys. **18**, 1040 (1950).
W. W. Wood and J. D. Jacobsen, J. Chem. Phys. **27**, 1207 (1957).
B. J. Alder and T. E. Wainwright, J. Chem. Phys. **27**, 1208 (1957).

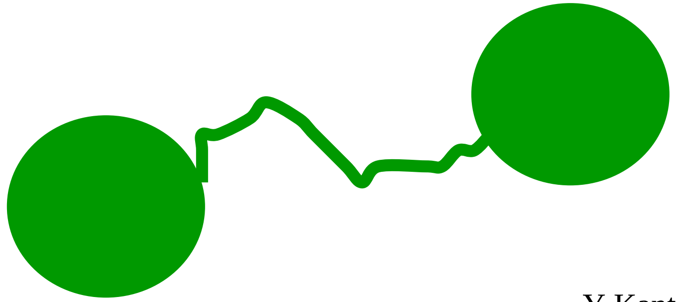
Potentials



Hard sphere repulsion

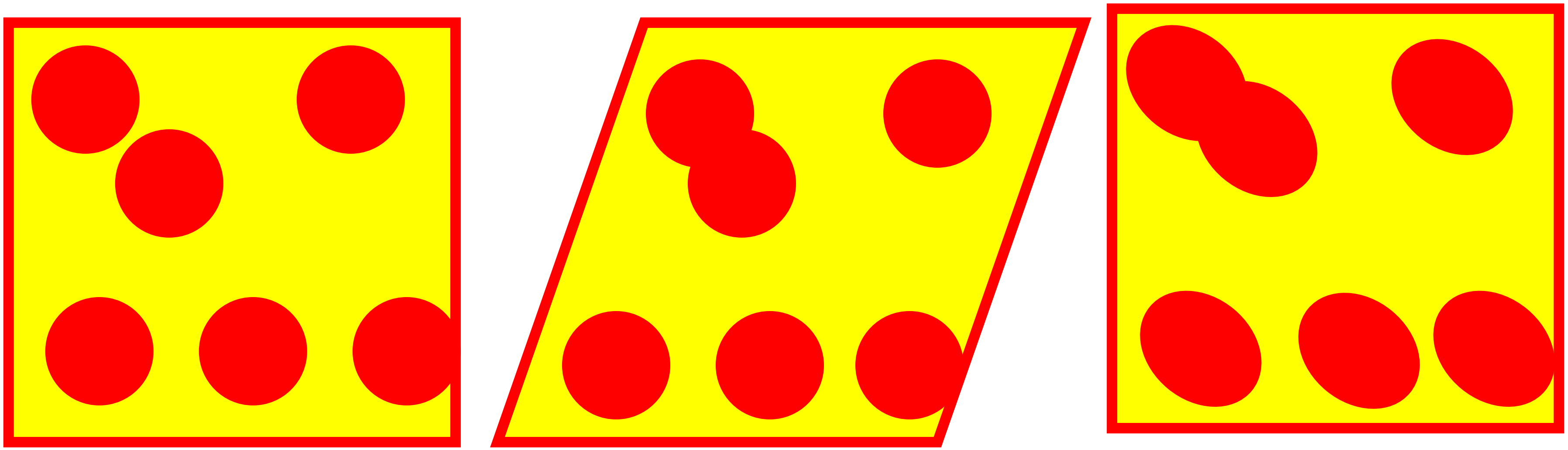


Tethering potential



Y.Kantor,M.Kardar,D.R.Nelson, Phys.Rev.Lett .**57**, 791 (1986).

Calculation of Elastic Constants

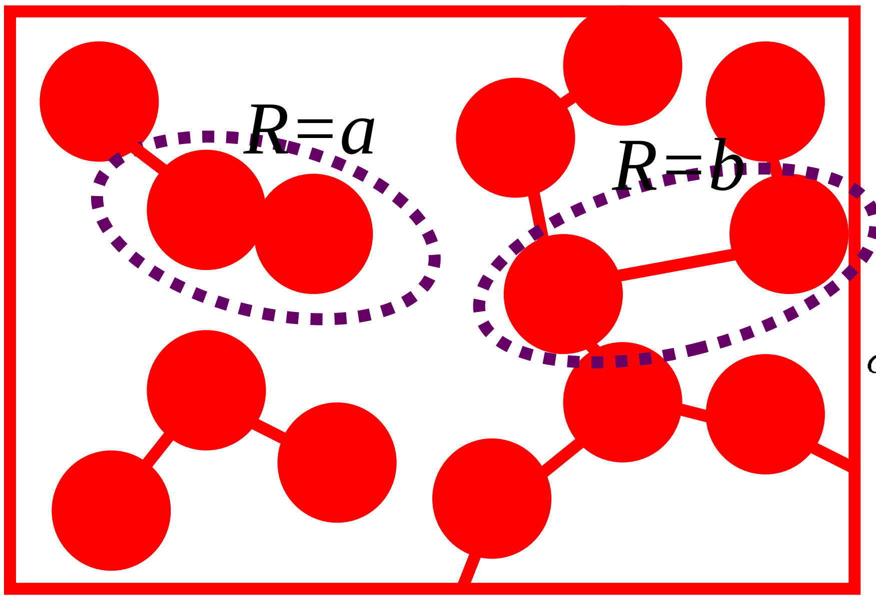


Unstrained state

Strained state

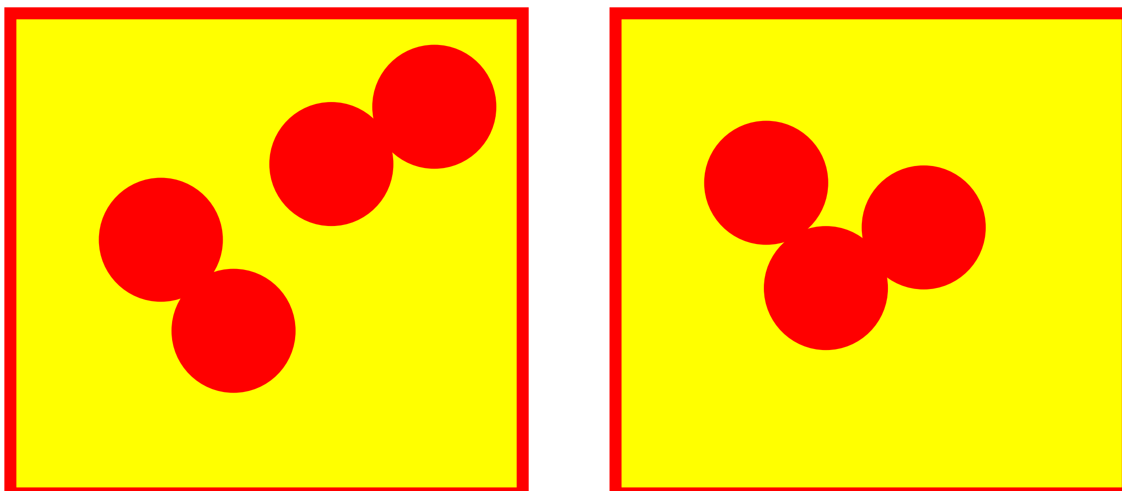
Boundaries restored to original state

Stress and elastic constants for "hard potentials"



J.A.Barker,D.Henderson
Mol.Phys.**21** (1971)

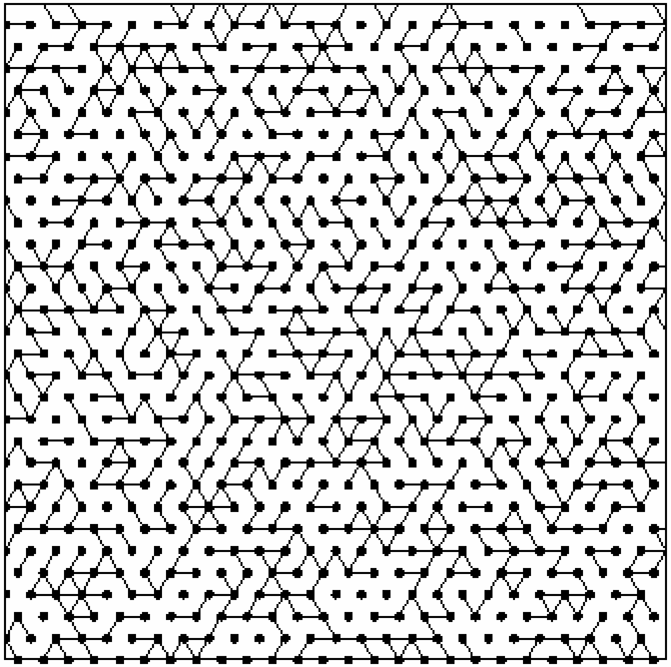
$$\sigma_{ij} = -\frac{kT}{V}\left[\left\langle \sum_{\text{pairs}} \frac{R_i R_j}{R}\delta(R-a) - \sum_{\text{bonds}} \frac{R_i R_j}{R}\delta(R-b) \right\rangle + N_{\text{atoms}}\right]$$

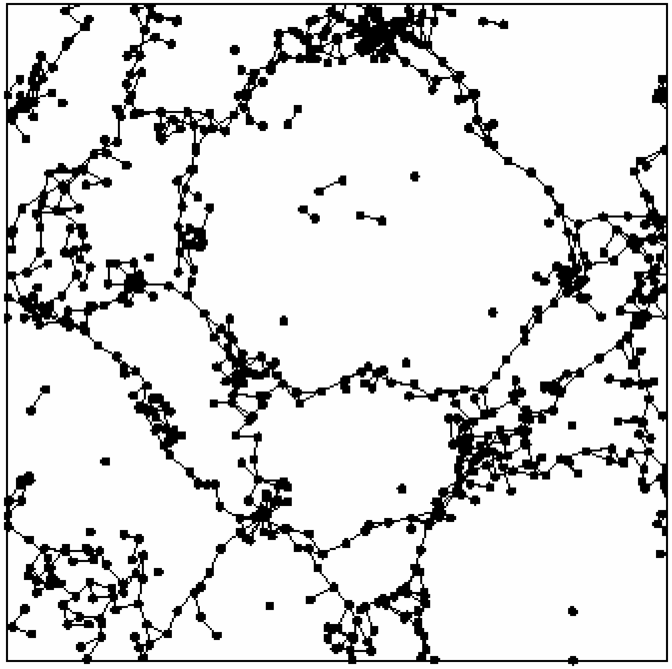


Elastic constants

O.Farago, Y.Kantor
Phys.Rev. E**61** (2000)

Percolating phantom network in 2D

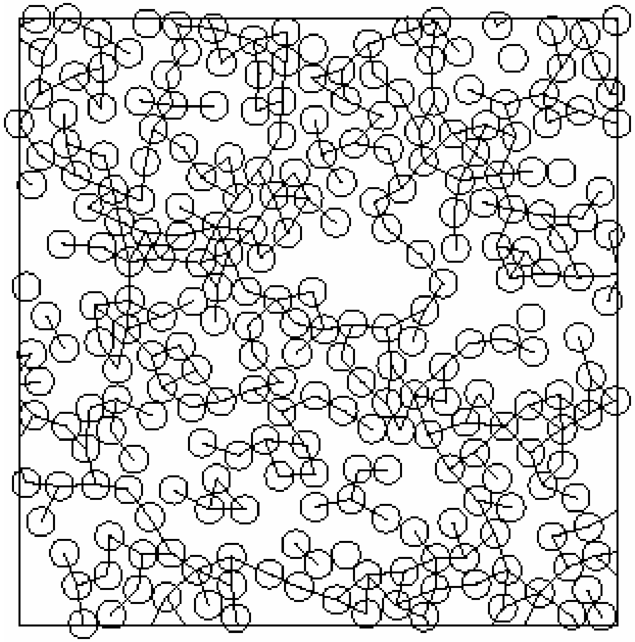




critical exponent 1.3

O.Farago, Y.Kantor
Europhys.Lett. **52** ,
413 (2000)

Percolation with excluded volume in 2D



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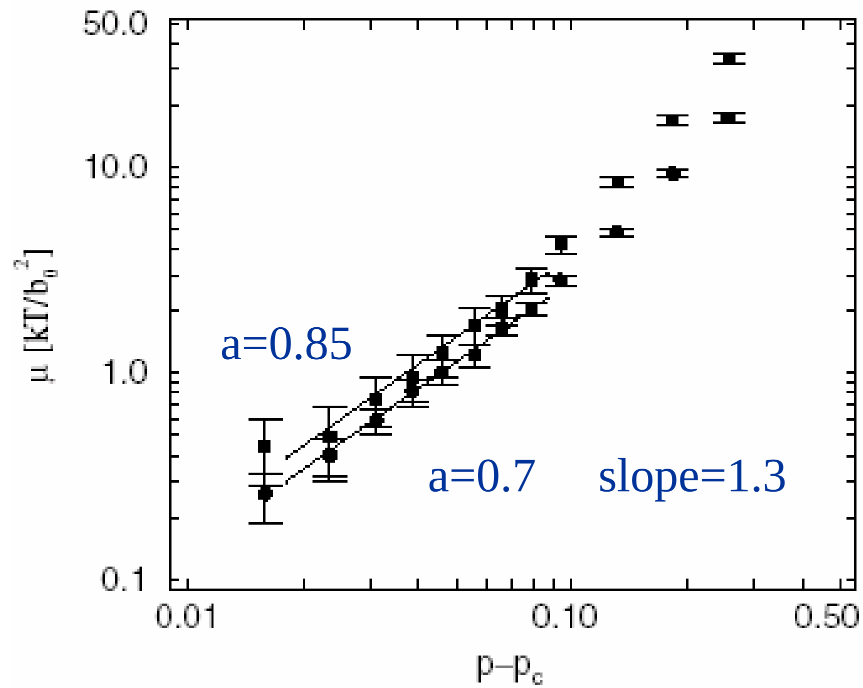
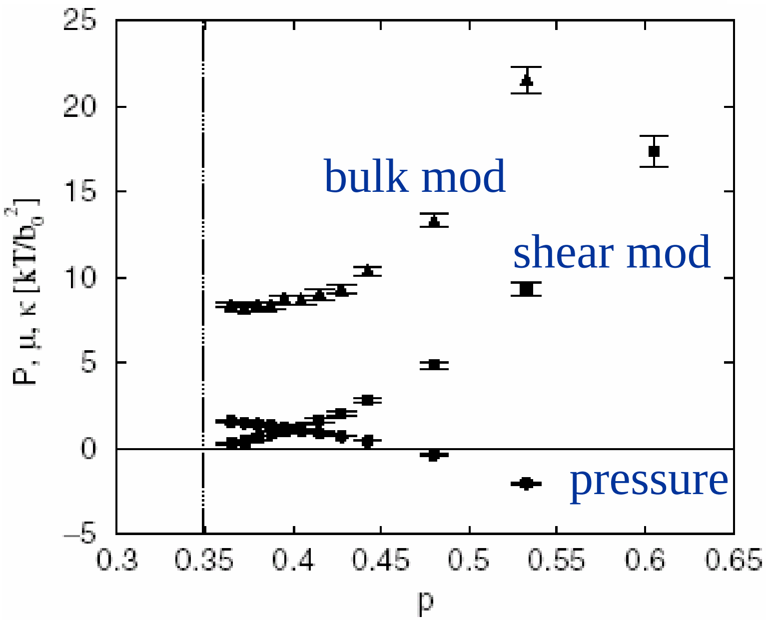
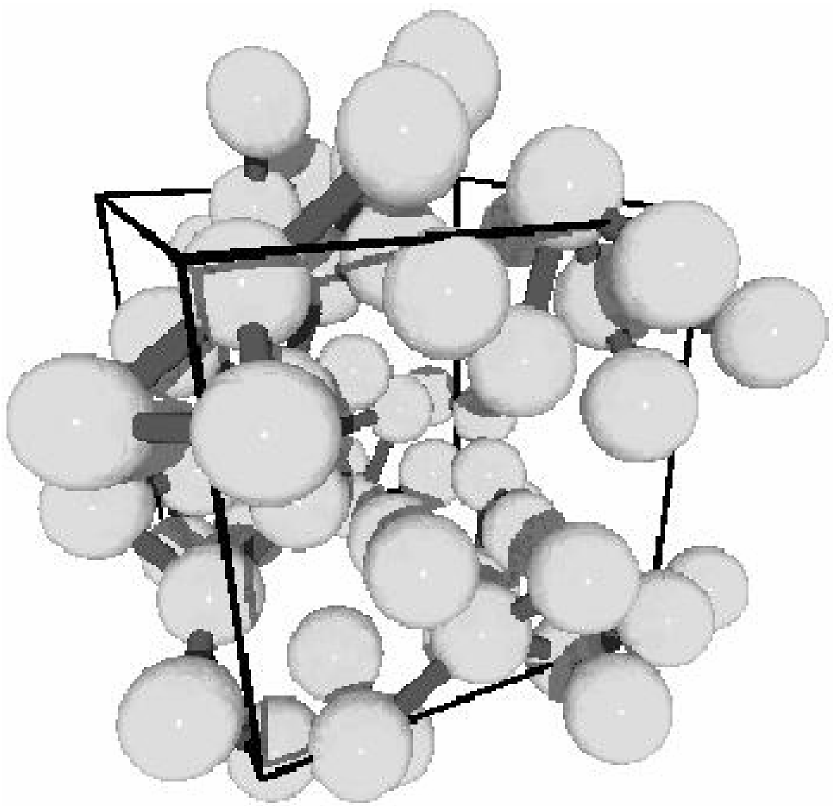
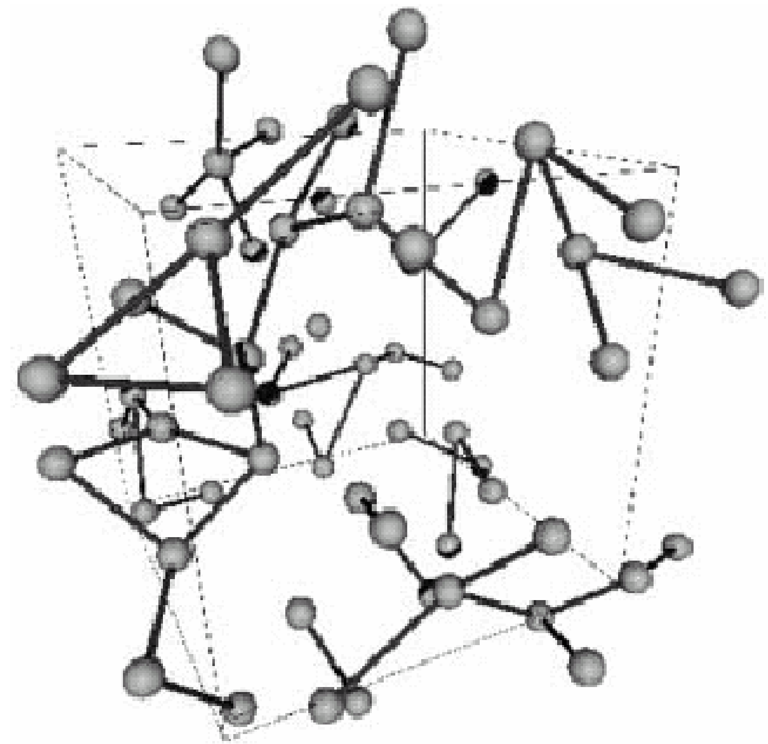




Percolation with excluded volume in 3D



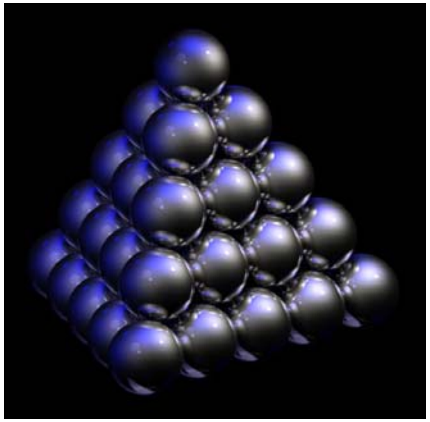


Actual size of excluded volume and size of the spheres reduced to 1/3 of their size

O.Farago, Y.Kantor
Europhys.Lett. **85**, 458 (2002)

critical exponent 2.0

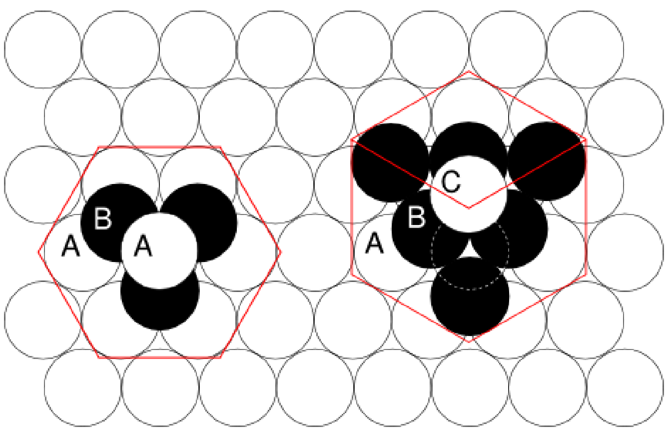
Dense hard sphere solids



1585 Harriot – cannonball arrangement
1611 Kepler's conjecture
1831 Gauss' proof for periodic lattices
1998 Hales' proof(?) for general case

Highest density

$$\rho = \frac{\pi}{3\sqrt{2}} = 0.74048...$$

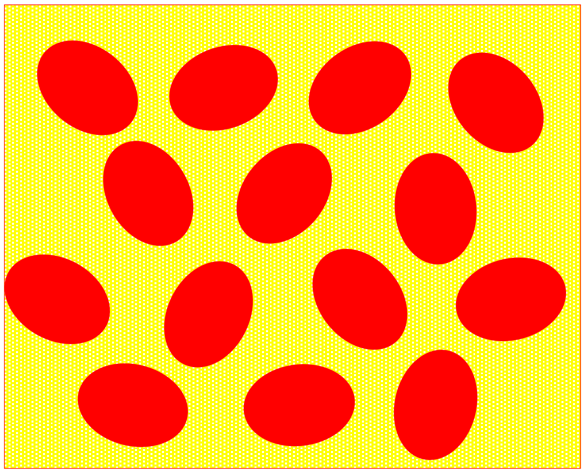


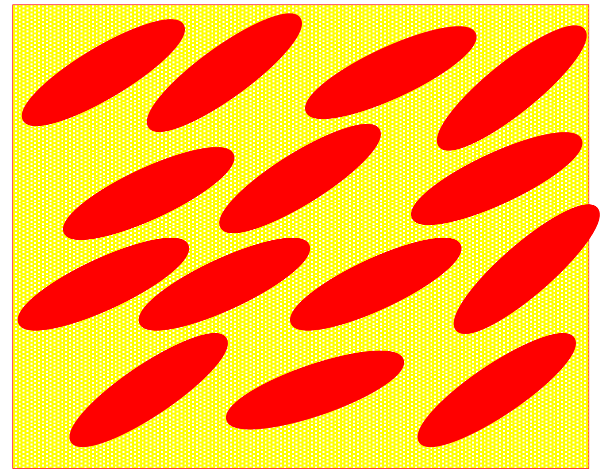
HCP **FCC**

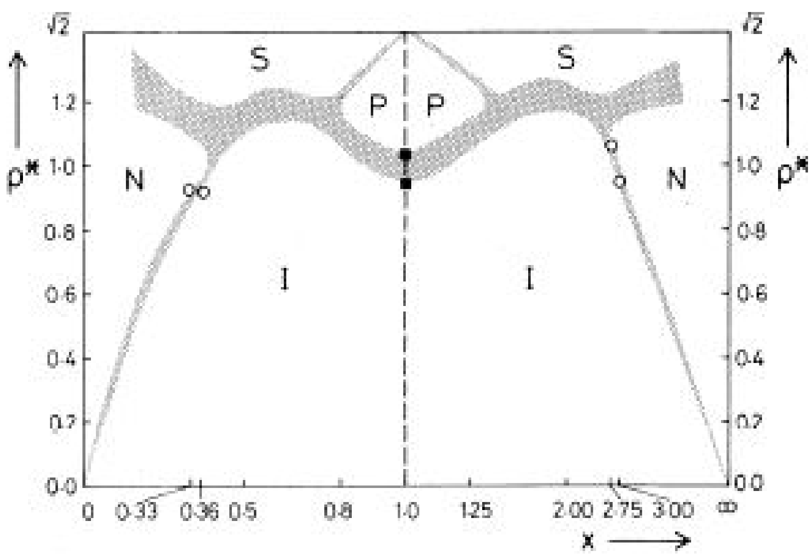
$$\Delta F \approx 0.001 N k_B T$$

Alder, B. J., Hoover, W. G. & Young, D. A. *J. Chem. Phys.* **49,**3688 (68)
Alder, B. J., Carter, B. P. & Young, D. A. *Phys. Rev.* **183,** 831(69).
Alder, B. J., Young, D. A., Mansigh, M. R. & Salsburg, Z. W.*J. Comp. Phys.* **7,** 361 (71).
Young, D. A. & Alder, B. J. *J. Chem. Phys.* **60,** 1254–1267 (1974).
Frenkel, D. & Ladd, A. J. C. *J. Chem. Phys.* **81,** 3188(84).
Bolhuis, P. G. & Frenkel, D. *J. Chem. Phys.* **106,** 666–687 (1997).
Mau S.-Ch. & Huse D.A., *Phys.Rev.* **E59,**4396-4401 (1999).

Spheroids – phase diagram



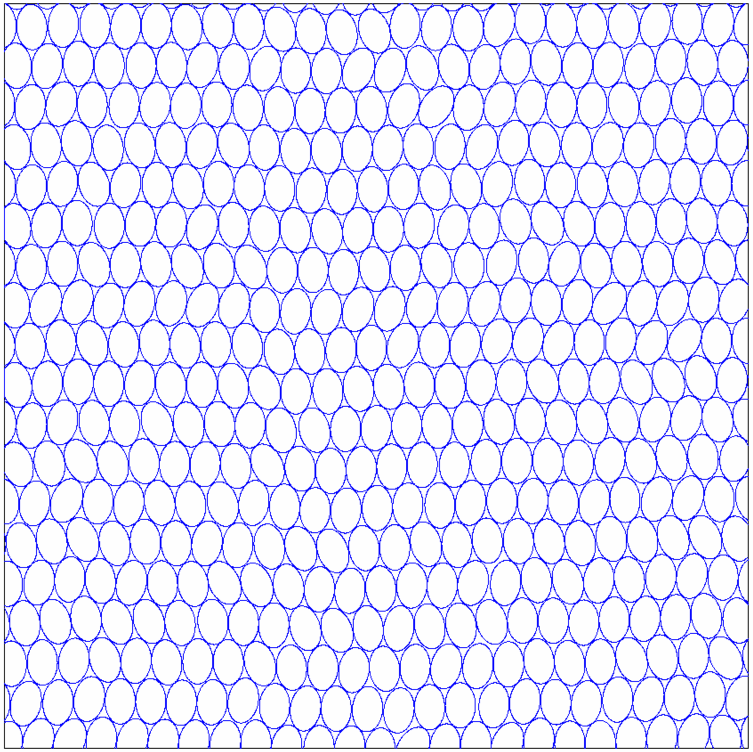


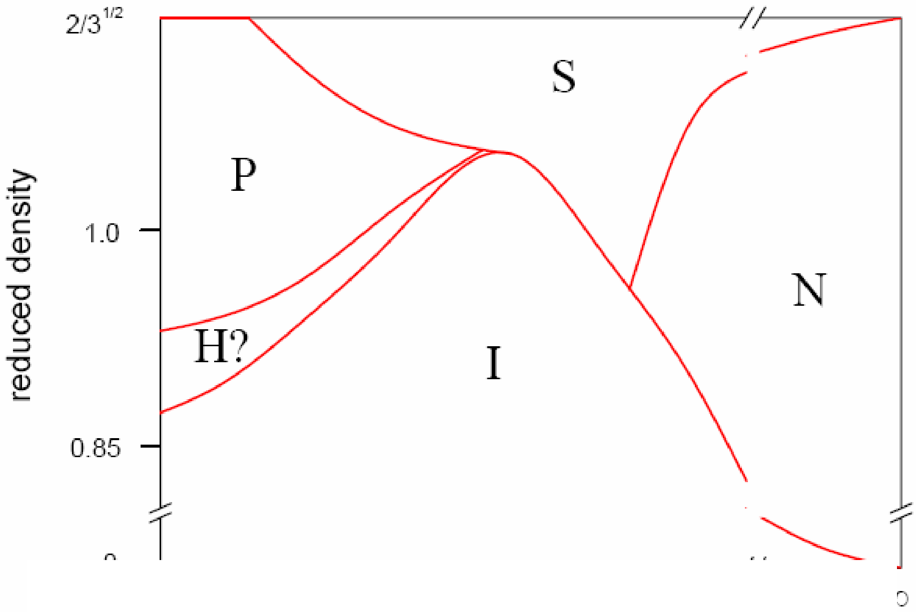


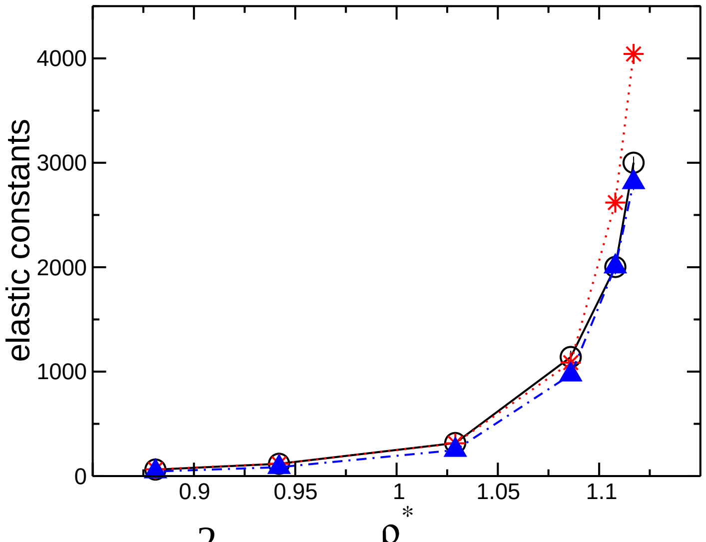
D.Frenkel, B.M.Mulder, J.P.McTague, PRL52,287 (1984)

Hard ellipses - 2D phase diagram

"Oriented" solid



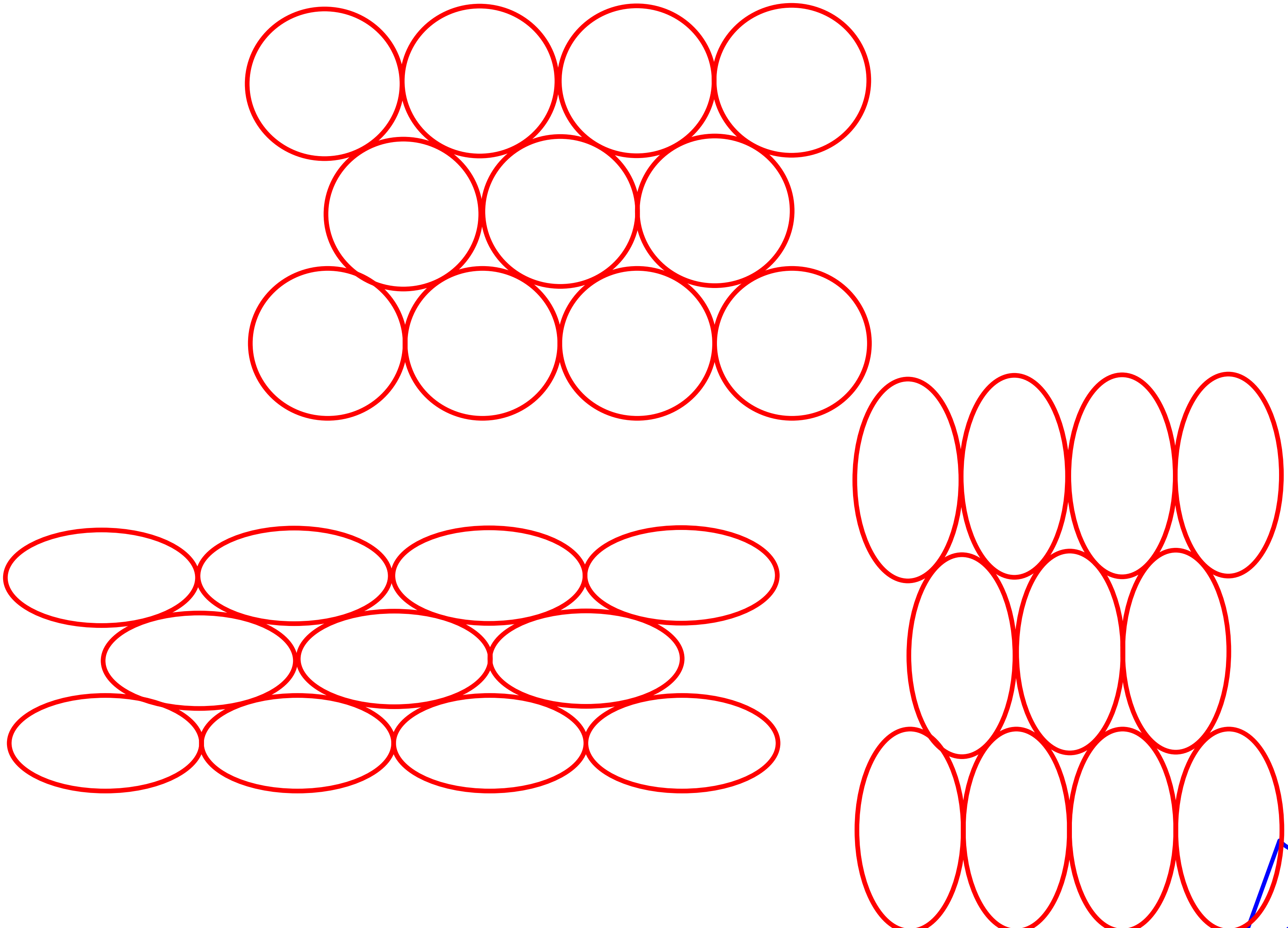




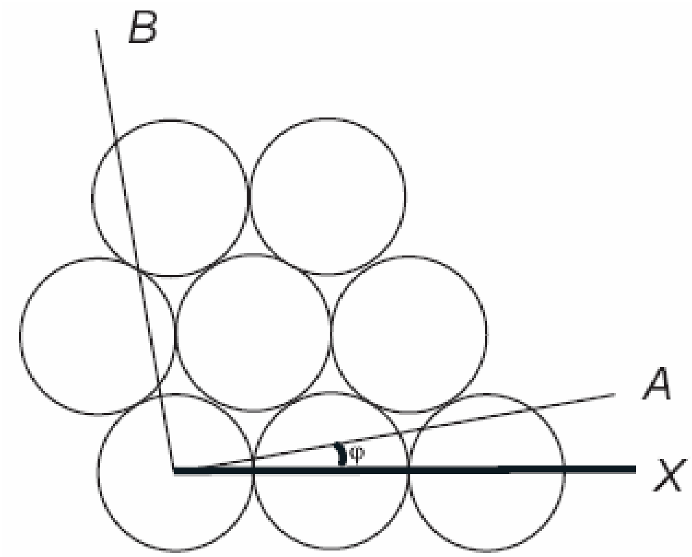
M. Murat, Y. Kantor, PRE74,031124 (2007)

$$\rho^* \equiv \rho \cdot 4ab, \quad \max \rho^* = \frac{2}{\sqrt{3}} \approx 1.155\ldots$$

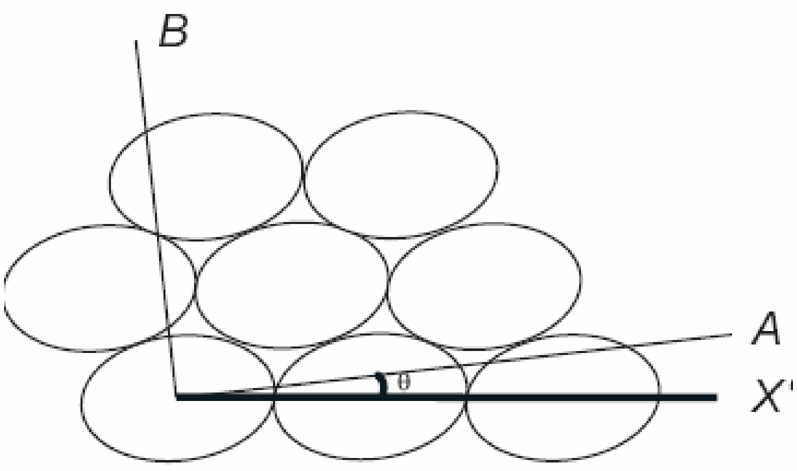
Possible dense states



Possible dense states (continued)

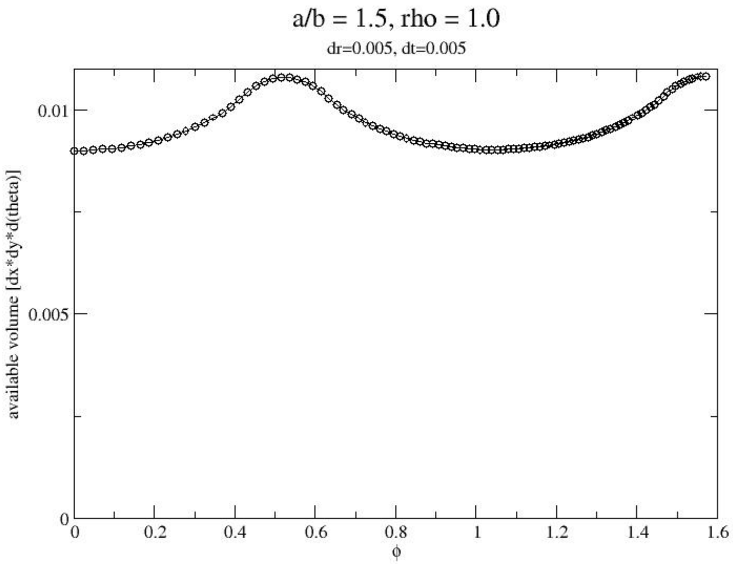


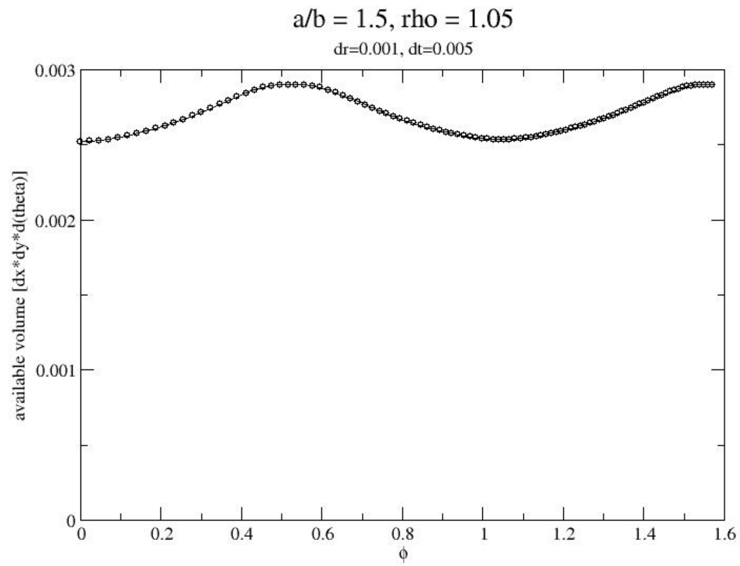
(a)

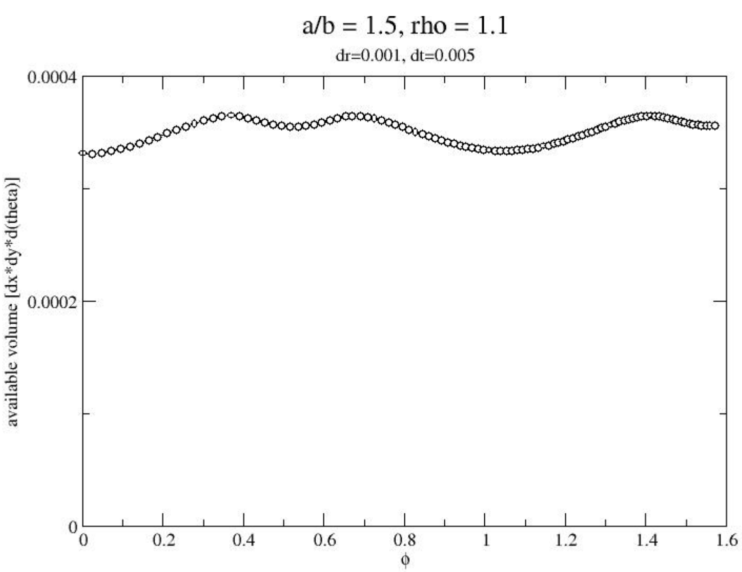


(b)

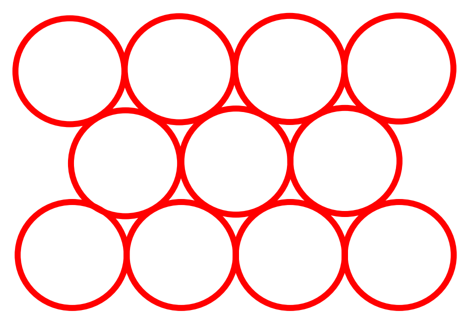
“MF” free energy dependence on the angle







$$\rho^* \equiv \rho \cdot 4ab, \quad \max \rho^* = \frac{2}{\sqrt{3}} \approx 1.155...$$



Conclusions

- *Direct calculation of elastic constants of hard potentials is possible*
- *Critical indices in 2D and 3D systems coincide with conductivity exponents (within the measurable range)*
- *Elasticity – useful tool in determining phase diagram*

That's all