Empty liquid phase of anisotropic particles

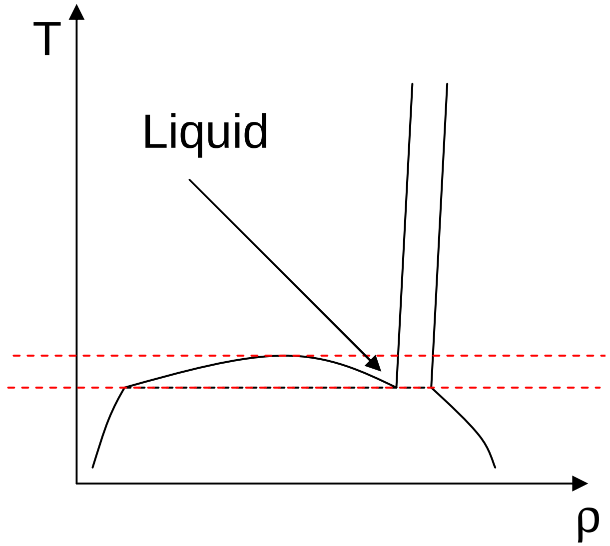
By Szabolcs Varga

Outline:

1) Critical temperature and volume fraction of VL phase coexistence
2) Phase behaviour of patchy spheres
3) Phase behaviour of Laponites
4) Phase behaviour of high valence square-well model
5) Predictions of van der Waals theory

CENTRAL EUROPEAN
STATISTICAL MECHANICS
MINI-MEETING
JUNE 12 - 13, 2014
BUDAPEST

Tenuous liquid



Properties

1) It flows like a gas
2) It occupies a particular volume
3) It does not expand

"If liquids were not common in everyday life, it is quite possible that theory would not yet have predicted their existence." Poon, Pusey and Lekkerkerker (Physics World, April 1996)

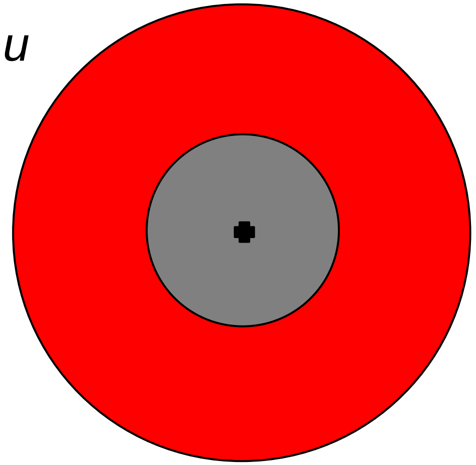
What are the conditions for the liquid state to occur?

1) Attraction
2) Short ranged repulsion

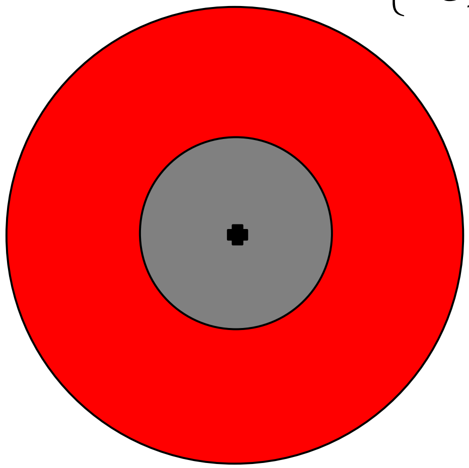
Hard sphere square well pair potential:

$$u^{HSSW}(r_{12}) = \begin{cases} \infty, & 0 \le r_{12} \le D \\ -\varepsilon, & D < r_{12} \le \tau D \end{cases}$$

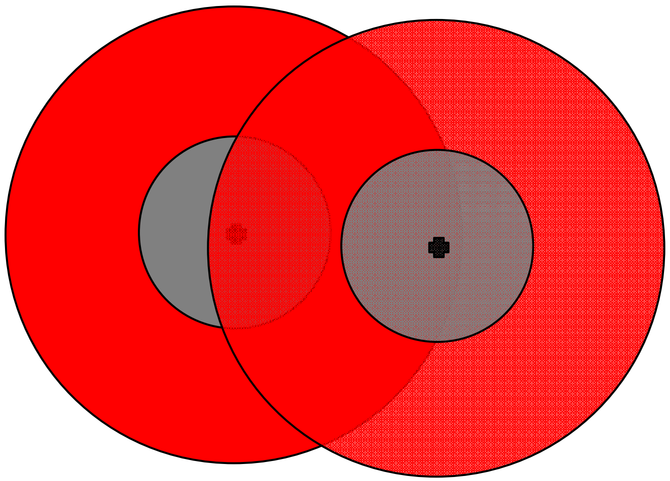
Pair potential: *u*



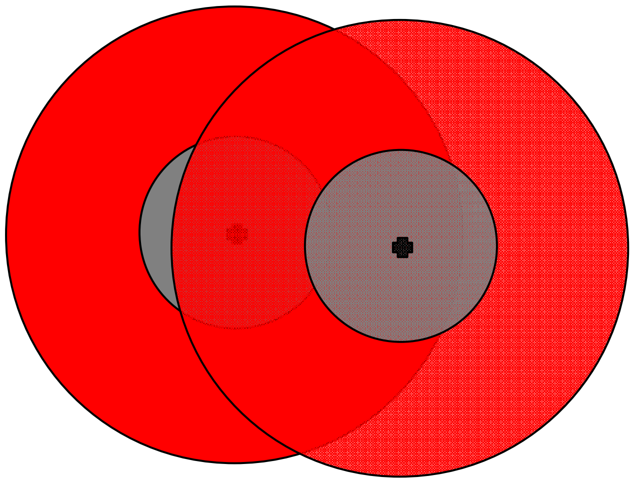
$u = 0$



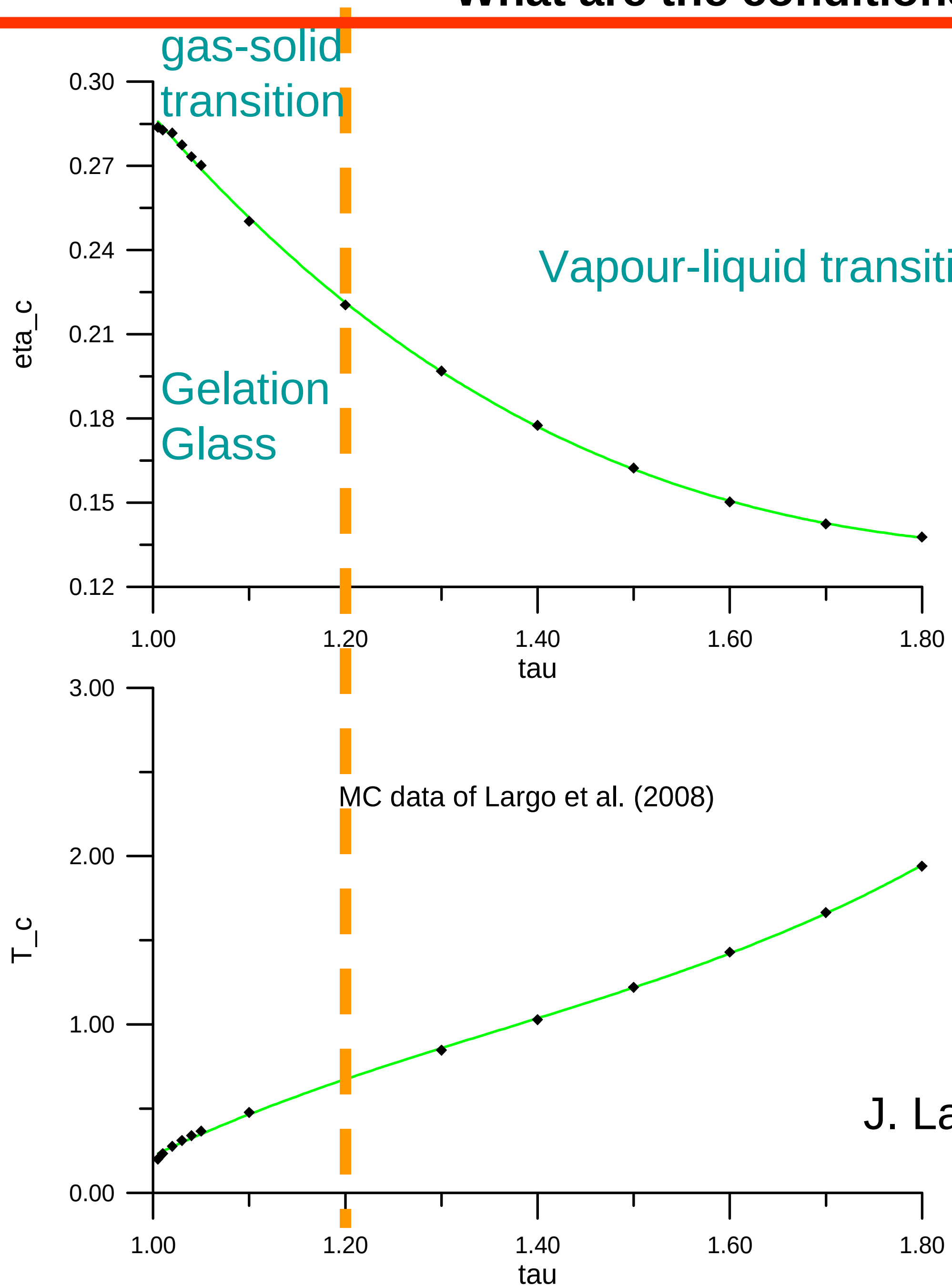
$u = -\varepsilon$



$u = \infty$



What are the conditions for the liquid state to occur?

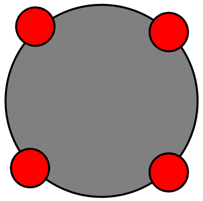


The range of the attraction must exceed a minimum value to have vapour-liquid transition.

J. Largo et al., JCP, 128, 134513 (2008)

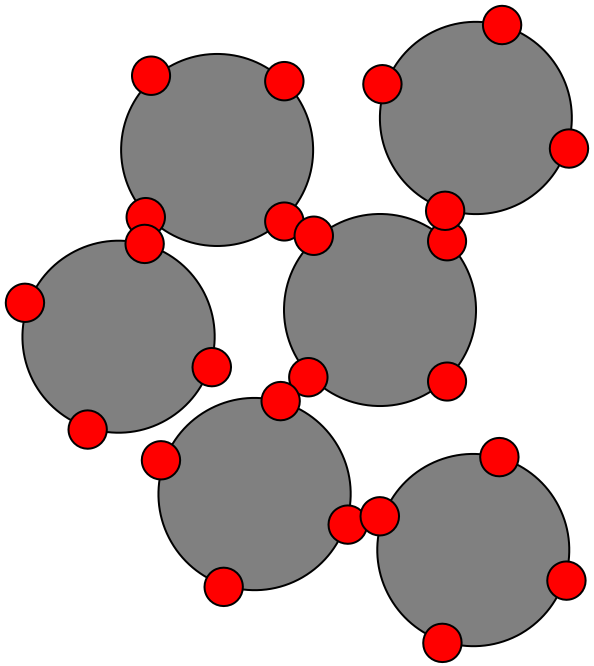
The effect of the anisotropy of the attraction

Patchy hard spheres:

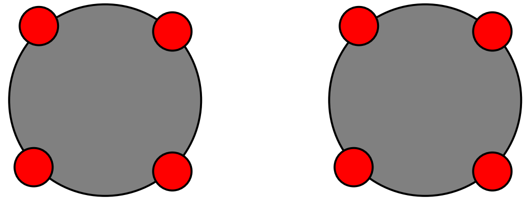


M=4 (number of sites)

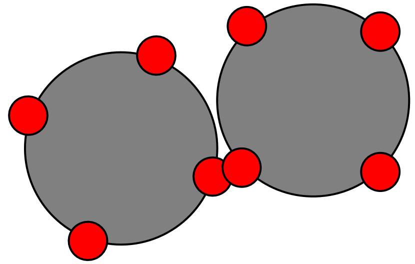
Liquid phase:



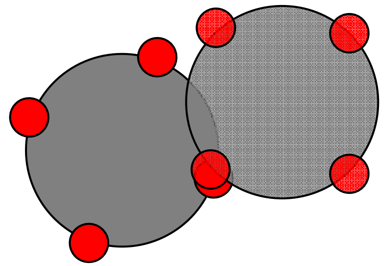
$u = 0$



$u = -\varepsilon$

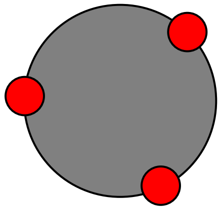


$u = \infty$

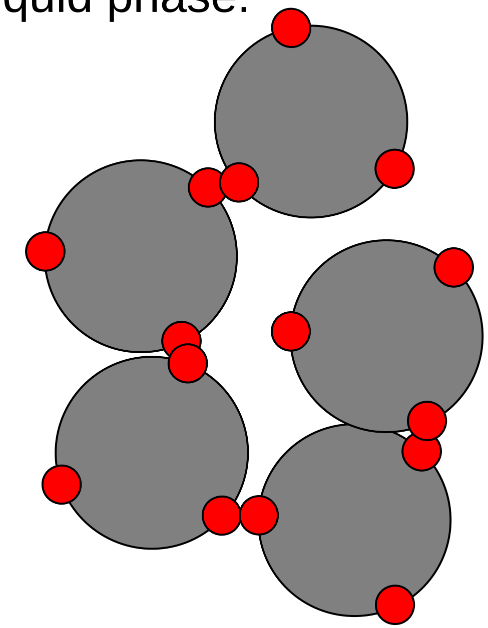


The effect of the anisotropy of the attraction

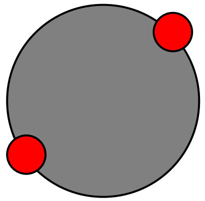
M=3



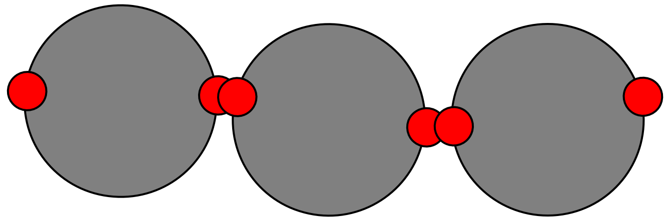
Liquid phase:

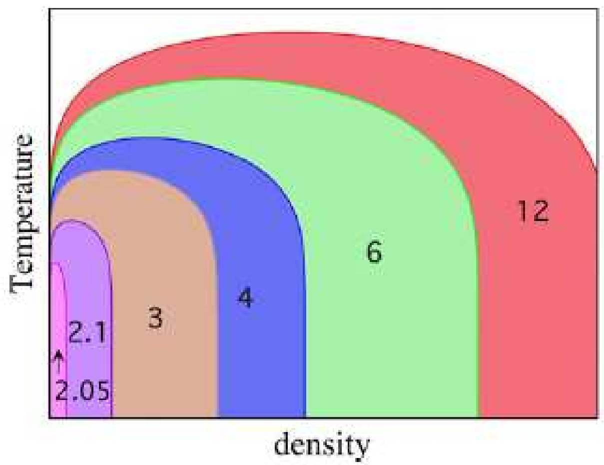


M=2



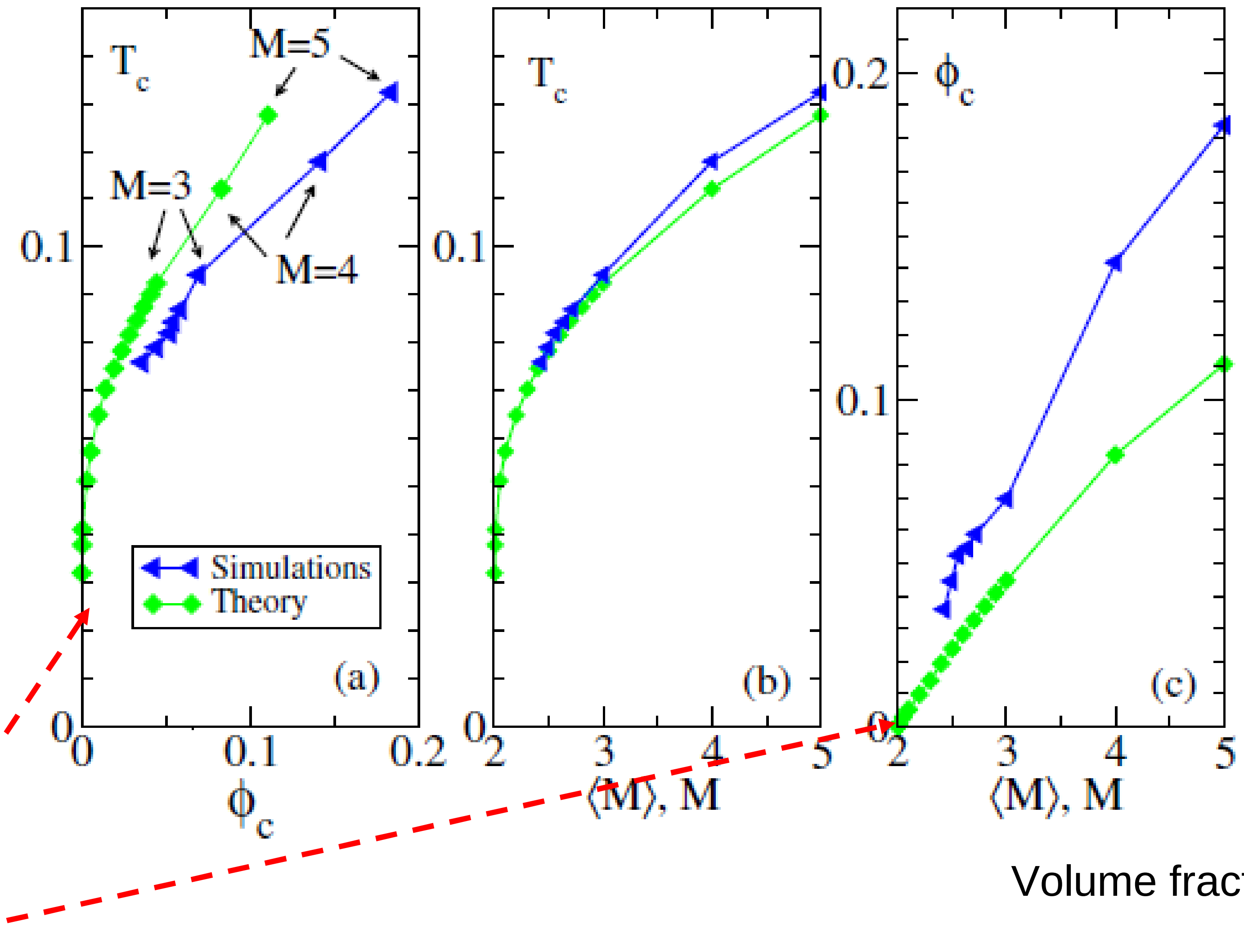
No liquid phase, but it forms chains.





E. Bianchi et al., PRL, 97, 168301 (2006)

The effect of the anisotropy of the attraction

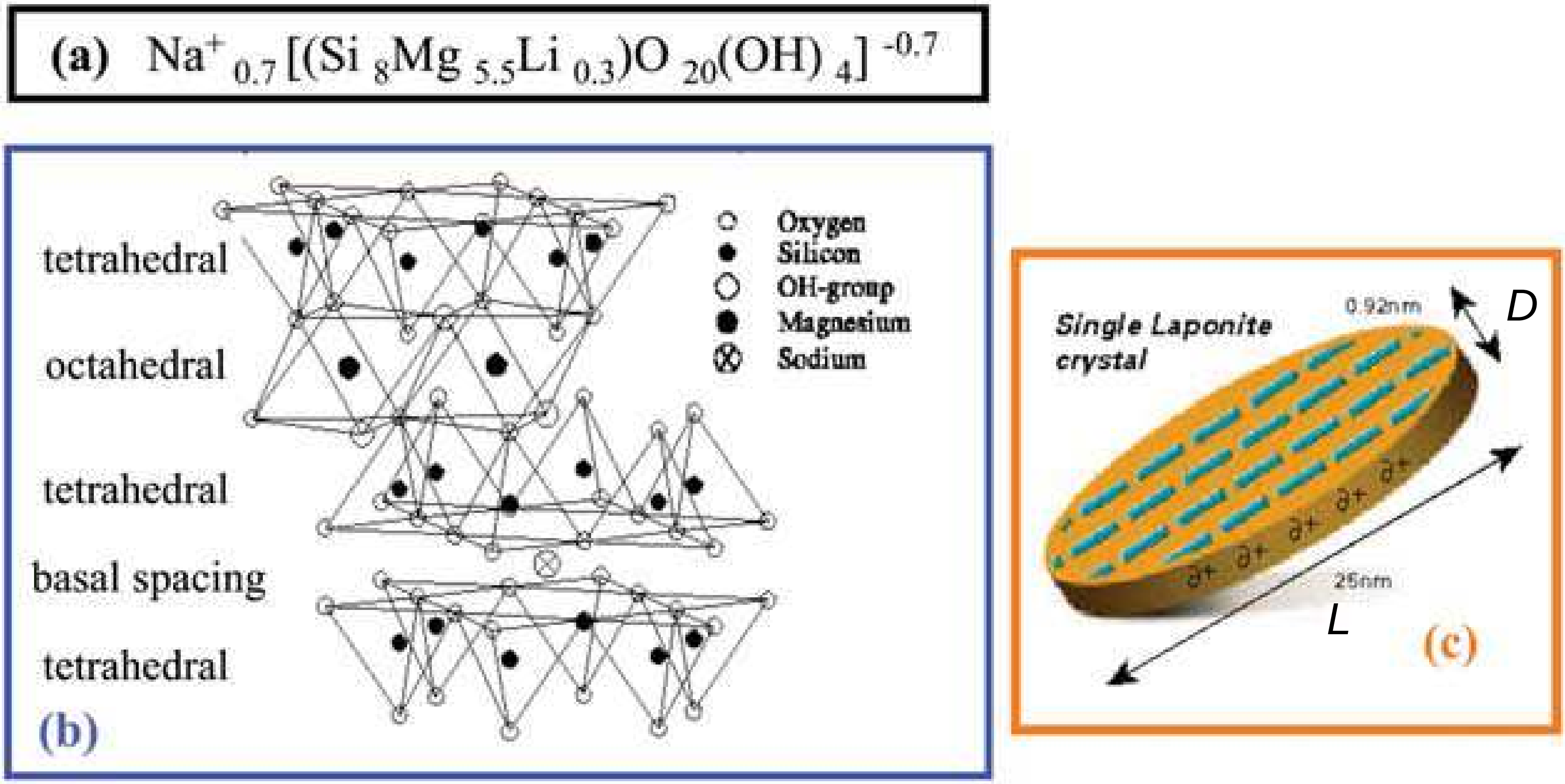


Volume fraction: $\phi = \rho v_{HS}$

Critical volume fraction goes to zero!!!!

E. Bianchi et al., PRL, 97, 168301 (2006)

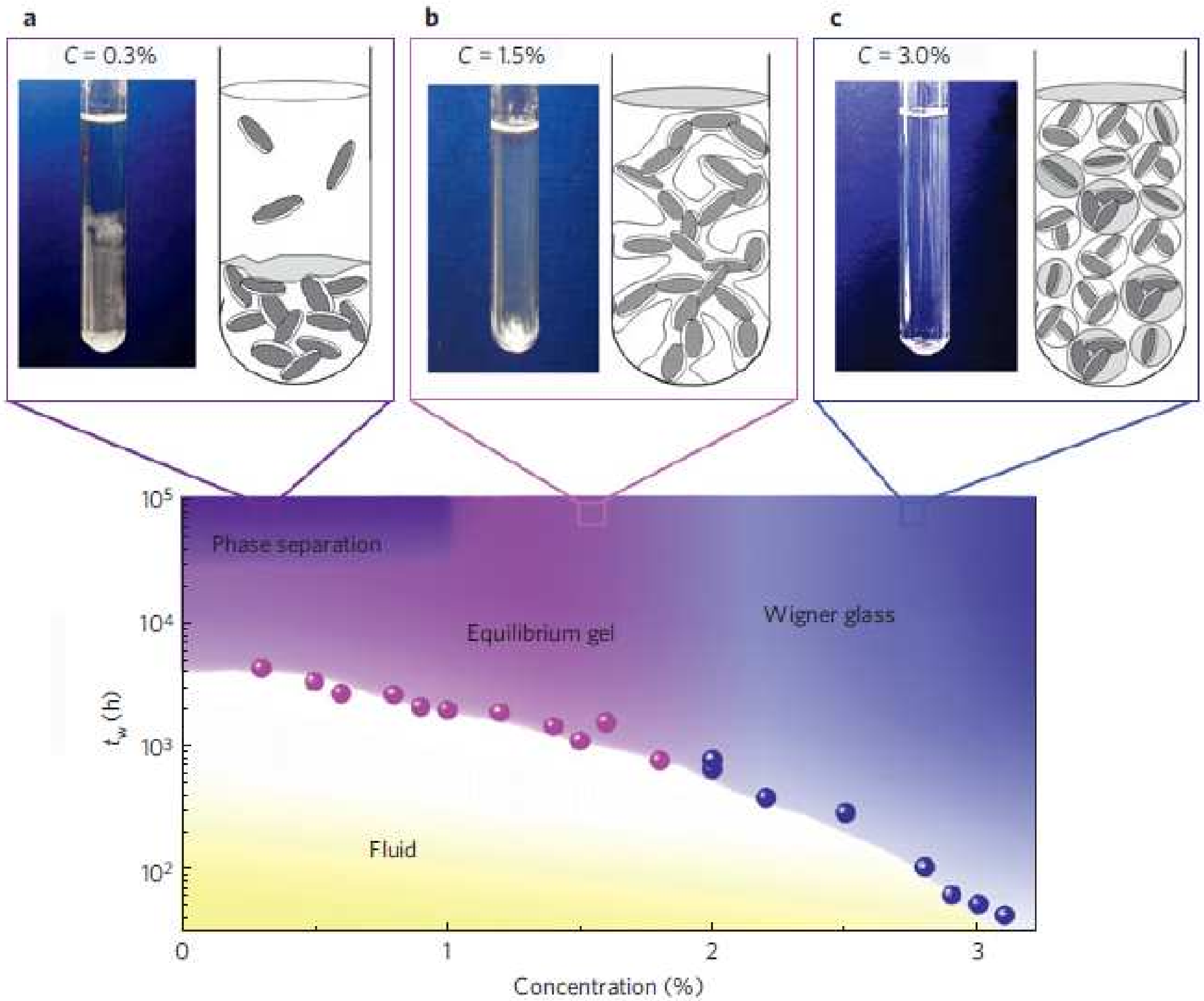
Structure of the Laponite



L/*D*=25

B. Ruzicka et al., Nature Materials, 10, 56 (2011)

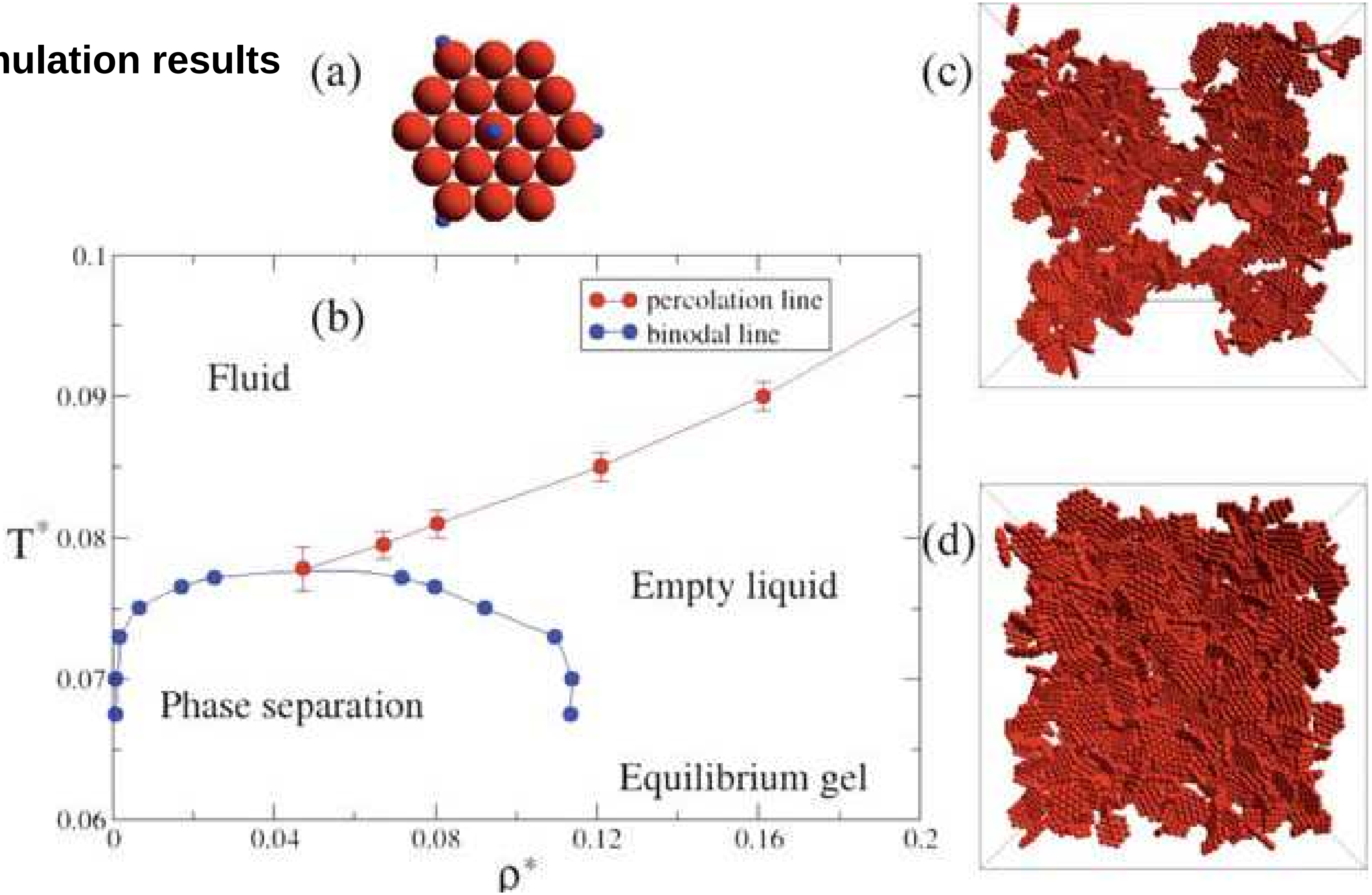
Experimental phase diagram



B. Ruzicka et al., Nature Materials, 10, 56 (2011)

Phase diagram of Laponites

Simulation results



B. Ruzicka et al., Nature Materials, 10, 56 (2011)

Ellipsoid model

Kappa (aspect ratio):

$$\kappa = \frac{\sigma_{\perp}}{\sigma_{\parallel}}$$

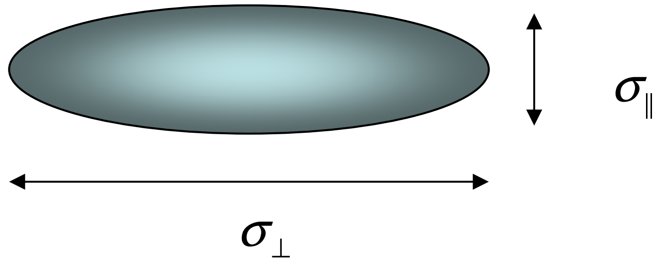
$$1 \; < \; \kappa \; < \; \infty$$

Hard sphere — Hard platelet

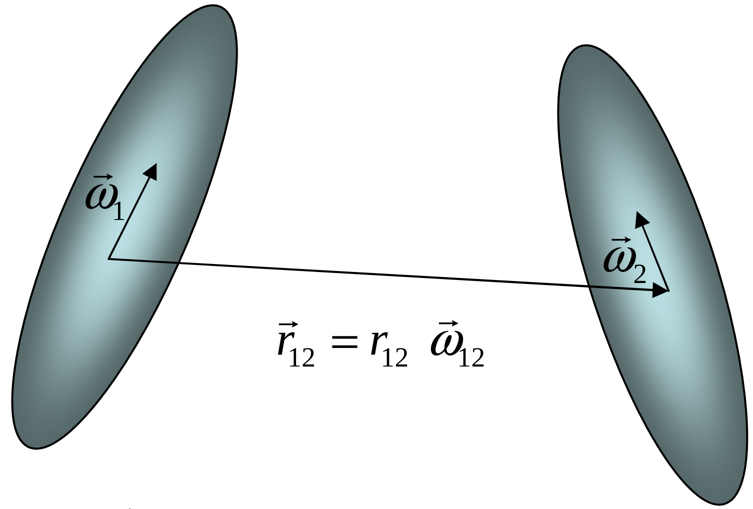
$$0 \; < \; \kappa \; < \; 1$$

Hard Needle — Hard sphere

Hard ellipsoid:



$\vec{\omega}_i$ -orientational unit vectors



Distance of closest approach

Pair potential:

$$u(r_{12}, \vec{\omega}_{12}, \vec{\omega}_1, \vec{\omega}_2) = \begin{cases} \infty, & 0 \le r_{12} \le \sigma(\vec{\omega}_{12}, \vec{\omega}_1, \vec{\omega}_2) \\ -\varepsilon, & \sigma(\vec{\omega}_{12}, \vec{\omega}_1, \vec{\omega}_2) < r_{12} \le \sigma(\vec{\omega}_{12}, \vec{\omega}_1, \vec{\omega}_2) + \lambda^* \end{cases}$$

$$\lambda^* = \lambda \min(\sigma_{\perp}, \sigma_{\parallel})$$

E. Meneses-Júarez, S. Varga, P. Orea and G. Odriozola, Soft Matter, 9, 5277 (2013).

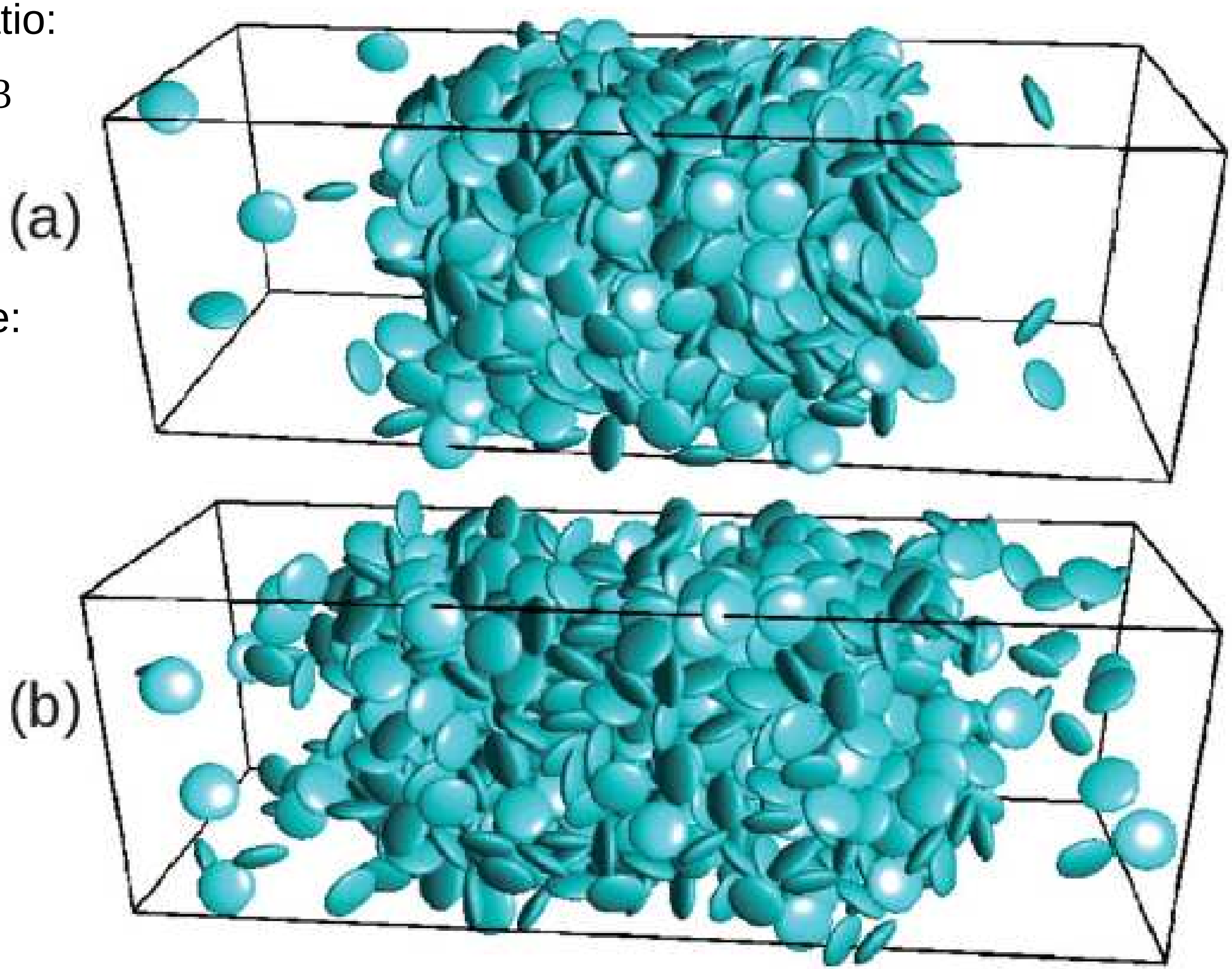
MC simulation results

Aspect ratio:

$$\kappa = \frac{\sigma_\perp}{\sigma_\parallel} = 3$$

SW range:

$$\lambda = 0.25$$

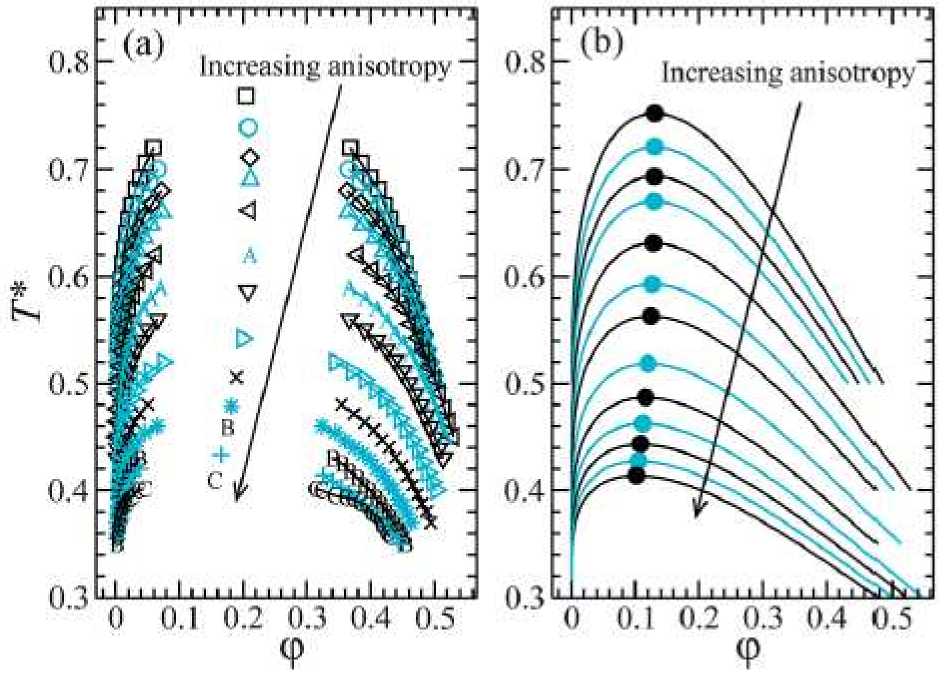


*T**=0.37

*T**=0.48

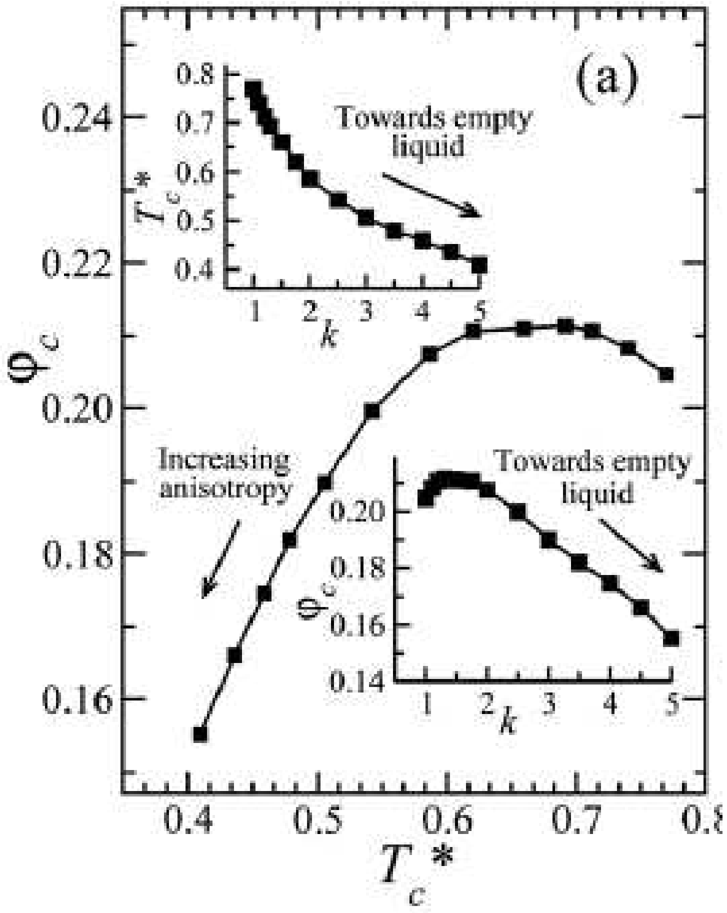
E. Meneses-Júarez, S. Varga, P. Orea and G. Odriozola, Soft Matter, 9, 5277 (2013).

Vapour-Liquid binodal of SWHE system



REMC DATA

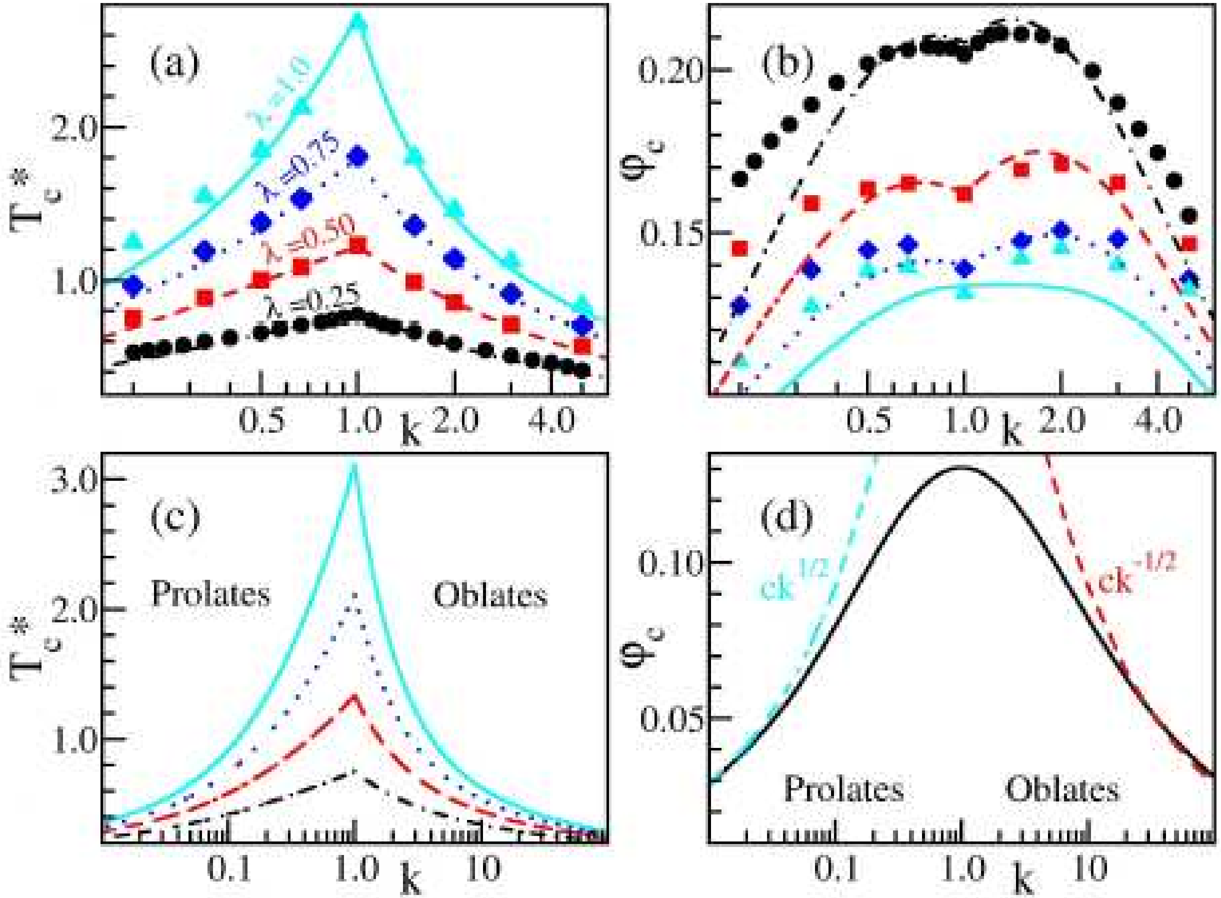
vW theory



Oblate ellipsoids

E. Meneses-Júarez, S. Varga, P. Orea and G. Odriozola, Soft Matter, 9, 5277 (2013).

Vapour-liquid phase coexistence SWHE system



vW theory

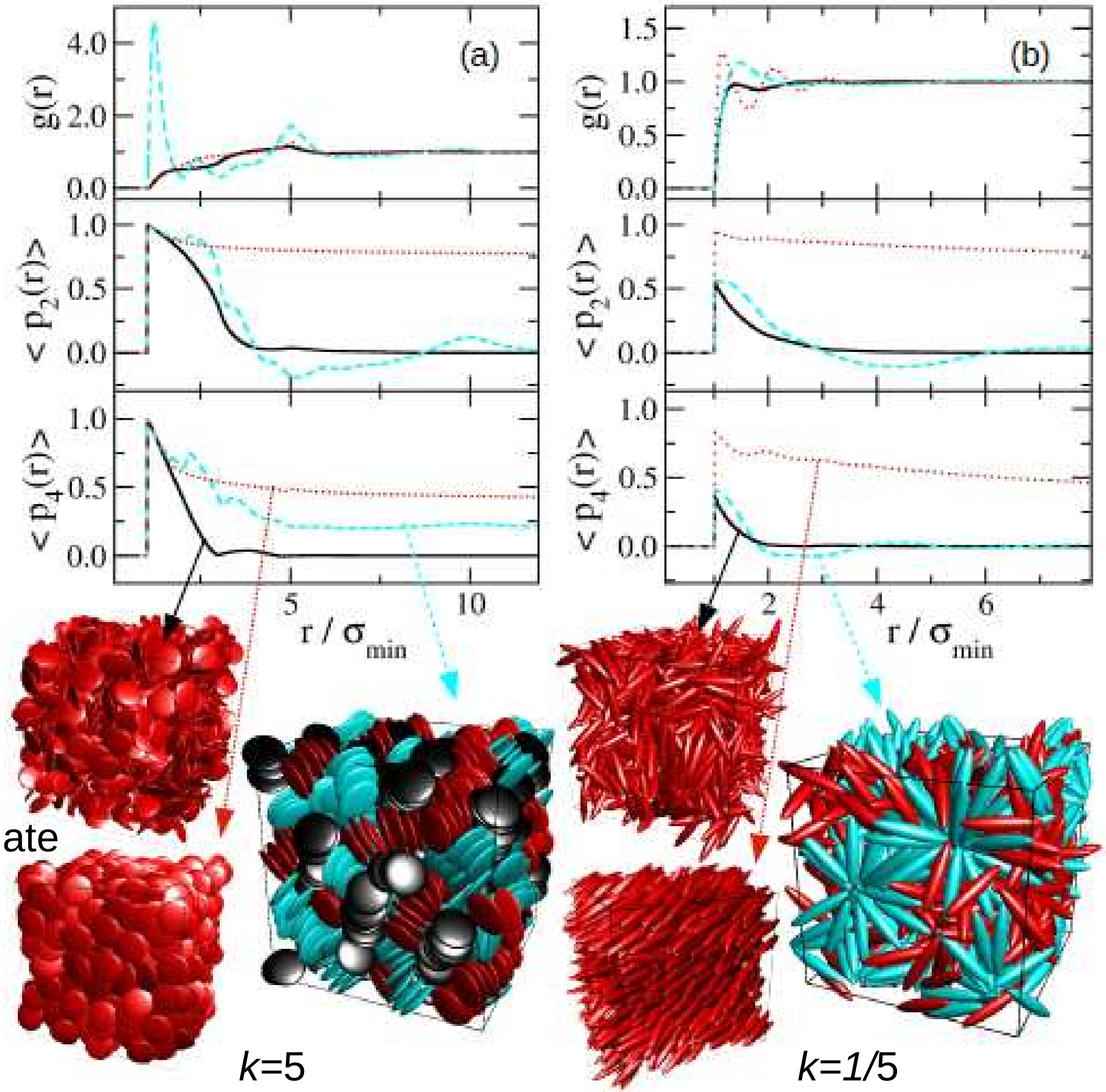
vW theory

S. Varga, E. Meneses-Juarez, and G. Odriozola, Soft Matter, 9, 11178 (2013)

Structure of the oblate/prolate ellipsoids

Positional and orientational radial distribution functions

$\alpha = 1$



isotropic
cubatic/aggregate
nematic

k=5

k=1/5

S. Varga, E. Meneses-Juarez, and G. Odriozola, Soft Matter, 9, 11178 (2013)

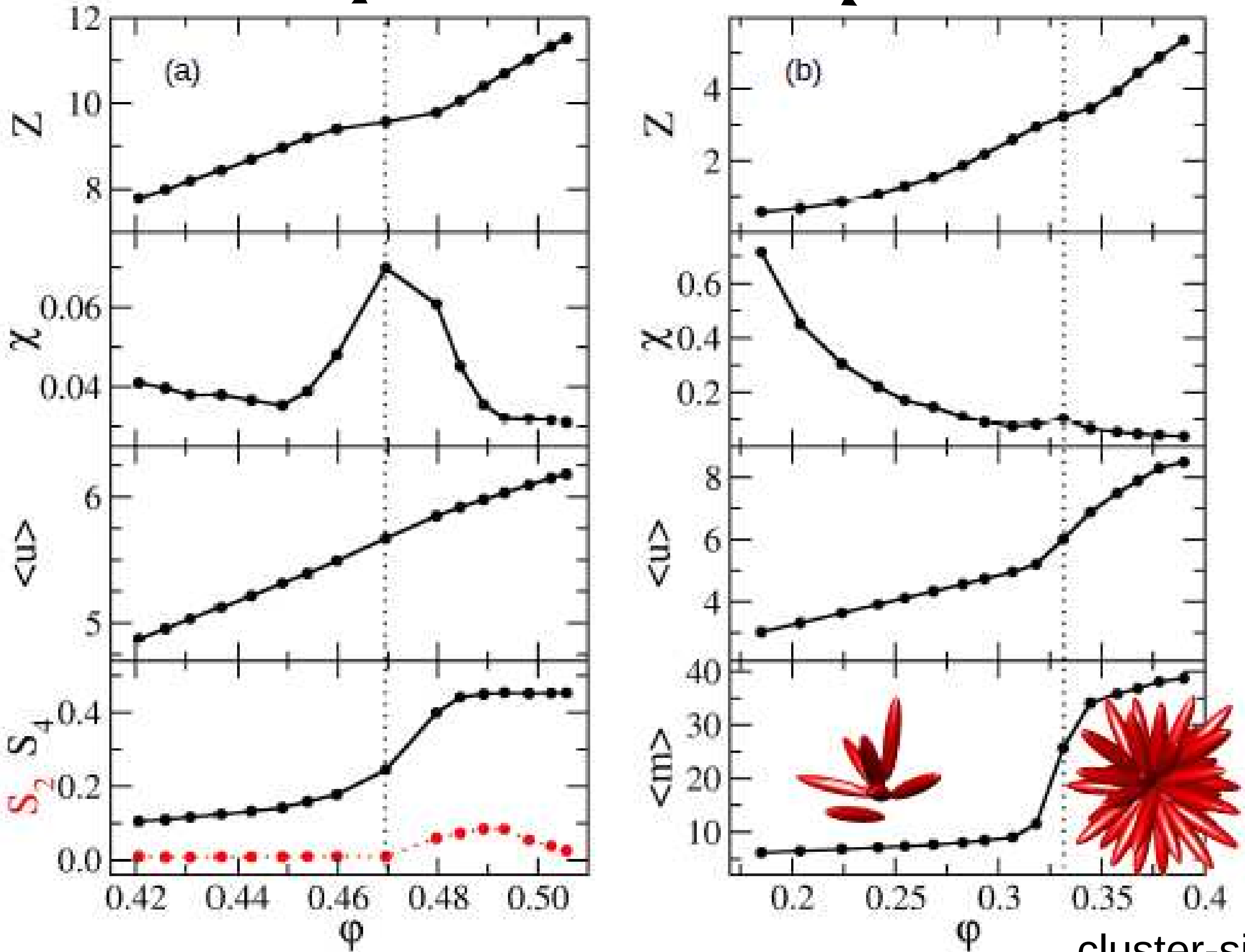
Structure of the oblate/prolate ellipsoids

$$Z = \beta P / \rho$$

$$\chi = \frac{\langle \rho^2 \rangle - \langle \rho \rangle^2}{\langle \rho \rangle^2}$$

|Potential energy|

Orientational order parameters



cluster-size

$T^* = 1.1, \alpha = 1, k = 5$

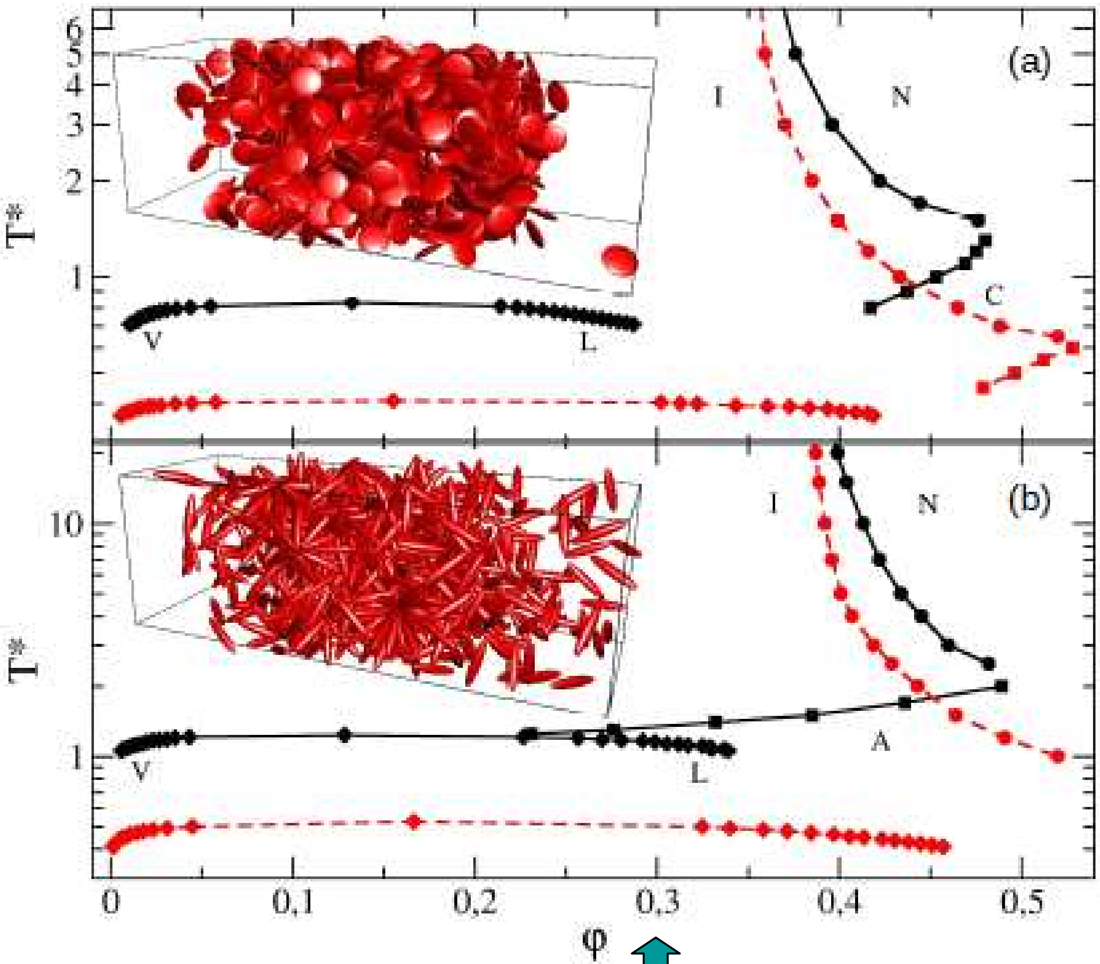
$T^* = 1.4, \alpha = 1, k = 1/5$

S. Varga, E. Meneses-Juarez, and G. Odriozola, Soft Matter, 9, 11178 (2013)

Phase diagram of the system of oblate ellipsoids for *k*=5

$\alpha = 1$

$\alpha = 0.25$

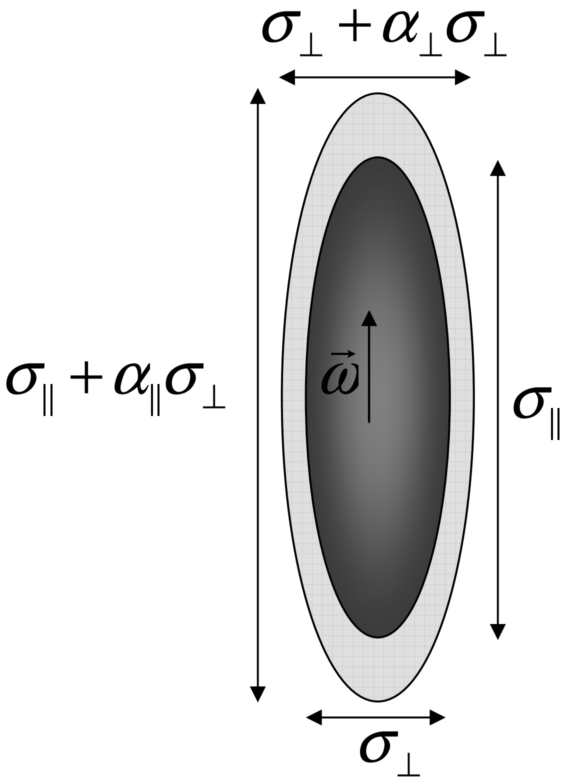


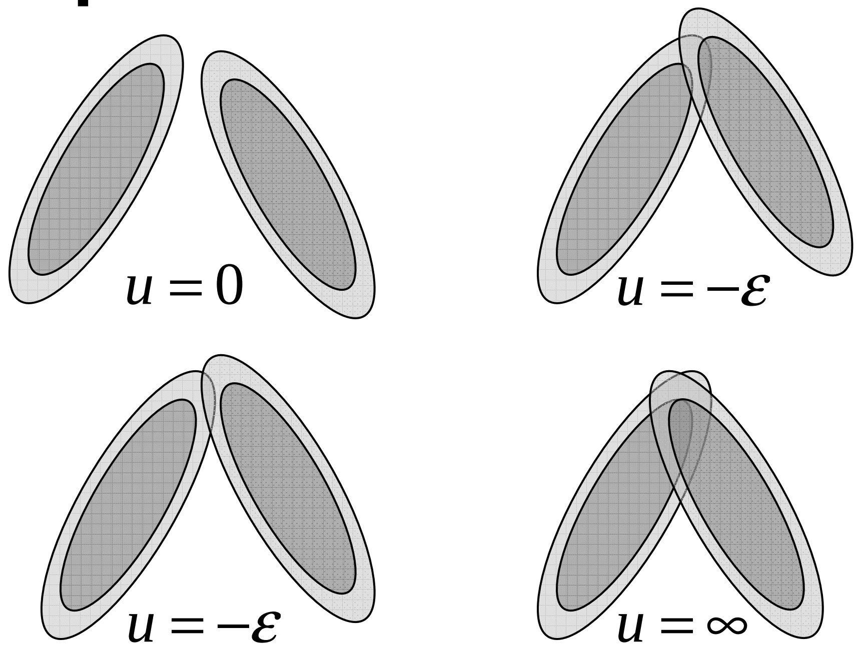
Phase diagram of the system of prolate ellipsoids for *k*=1/5

S. Varga, E. Meneses-Juarez, and G. Odriozola, Soft Matter, 9, 11178 (2013)

Generalised ellipsoidal model

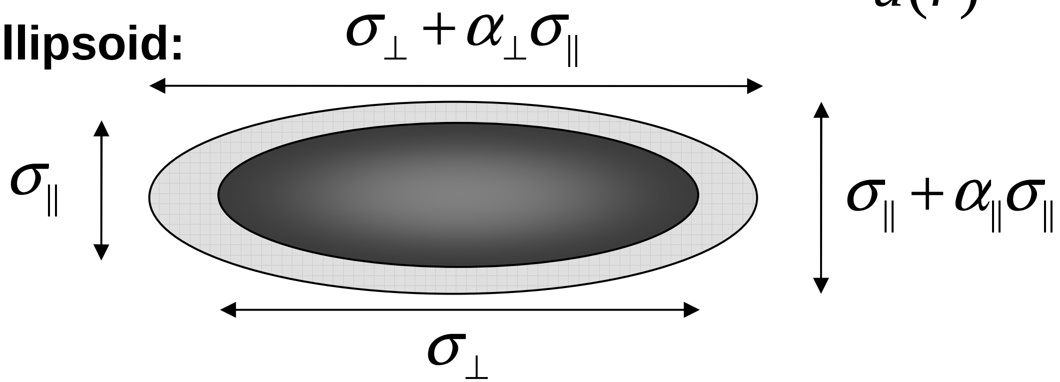
Prolate ellipsoid:



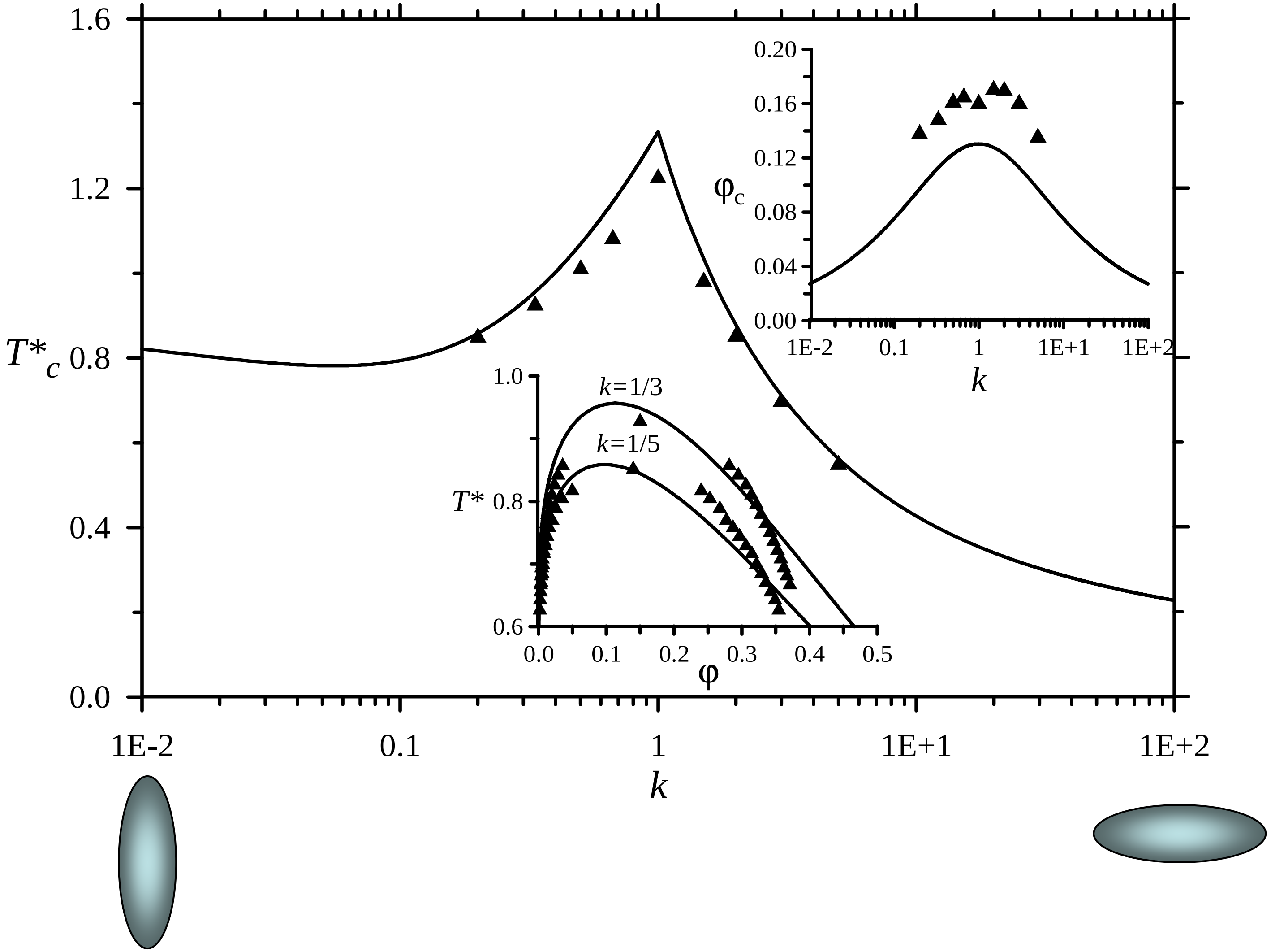


$$u(r) = \begin{cases} \infty, & r \le \sigma_I \\ -\varepsilon, & \sigma_I \le r \le \sigma_O \end{cases}$$

Oblate ellipsoid:

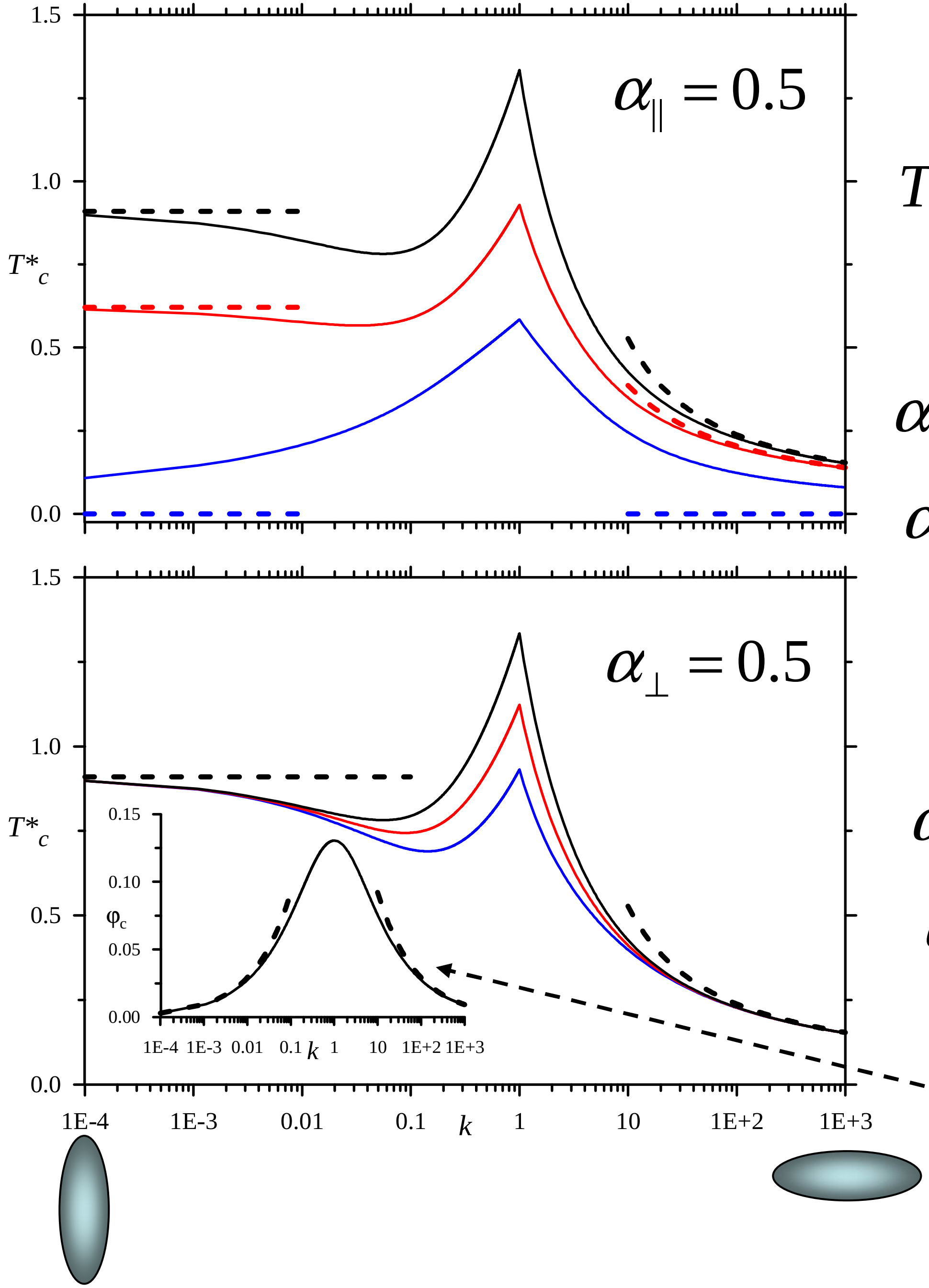


S. Varga, E. Meneses-Juarez, and G. Odriozola, Journal of Chemical Physics,140, 134905 (2014)



$$\alpha_{\parallel} = 0.5 \qquad \alpha_{\perp} = 0.5$$

S. Varga, E. Meneses-Juarez, and G. Odriozola, Journal of Chemical Physics,140, 134905 (2014)



Dashed curves:

$$T_c^* = \begin{cases} \ln^{-1}(1+1/\alpha_\perp), & k \to 0 \\ \ln^{-1}(k/3\alpha_\perp) = 0, & k \to \infty \end{cases}$$

$\alpha_\perp = 0.5$

↑

$\alpha_\perp = 0$

$\alpha_\parallel = 0.5$

↑

$\alpha_\parallel = 0$

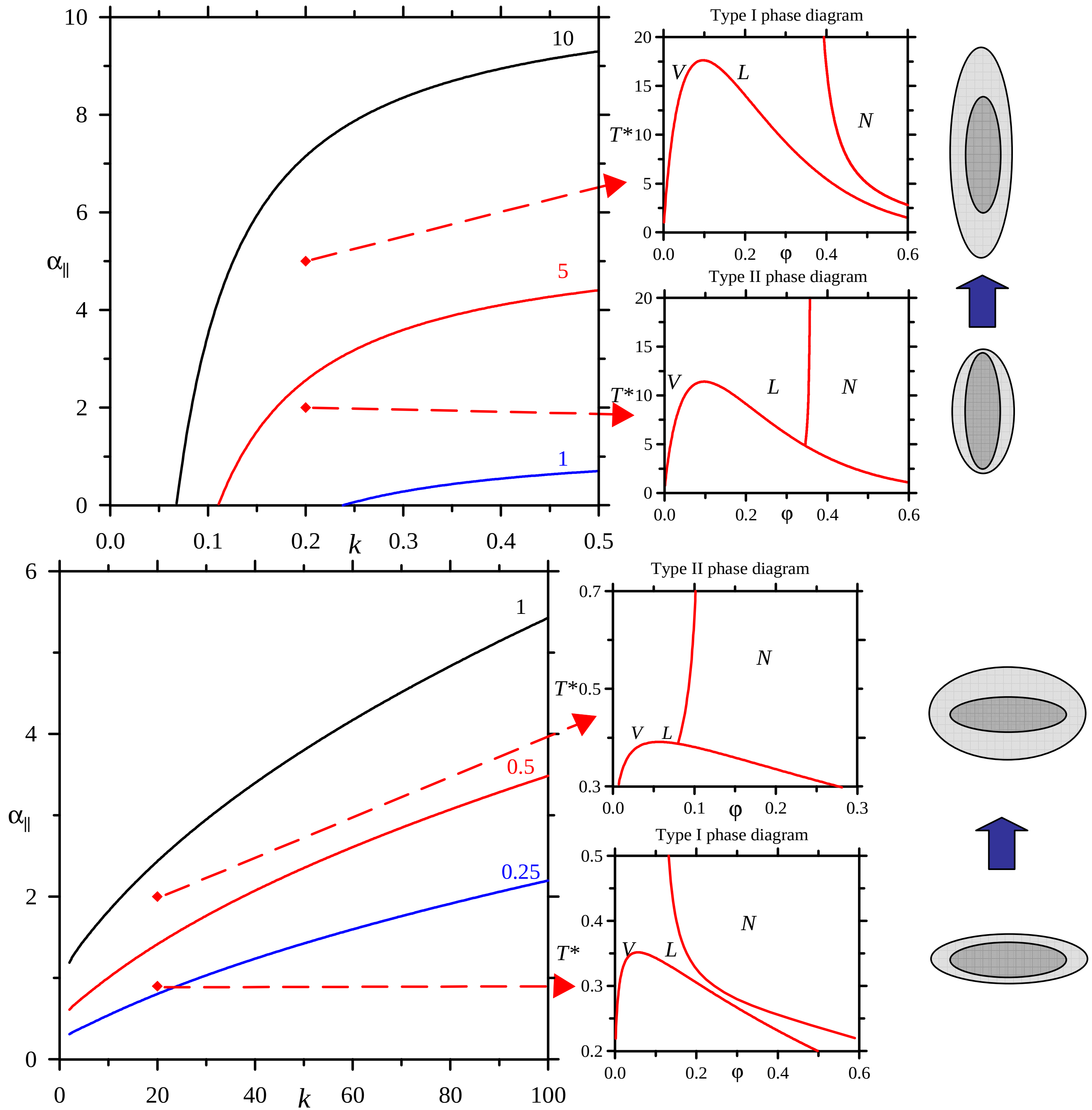
$$\varphi_c = \begin{cases} c/\sqrt{k}, & k \to \infty \\ c\sqrt{k}, & k \to 0 \end{cases}$$

where $c = 2/\sqrt{15\pi}$

S. Varga, E. Meneses-Juarez, and G. Odriozola, Journal of Chemical Physics,140, 134905 (2014)

Prolate

Oblate



S. Varga, E. Meneses-Juarez, and G. Odriozola, Journal of Chemical Physics,140, 134905 (2014)

(Thank you for your attention)