MESOSCOPIC THEORY OF PHASE TRANSITIONS IN COLLOIDAL SYSTEMS

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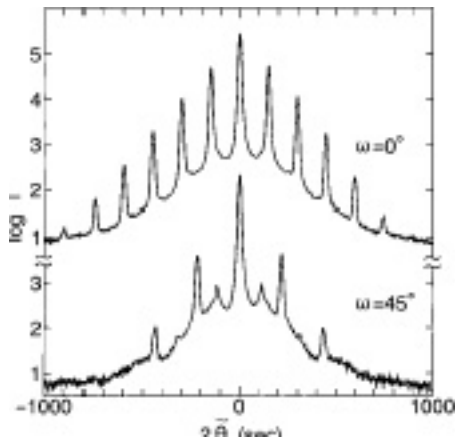
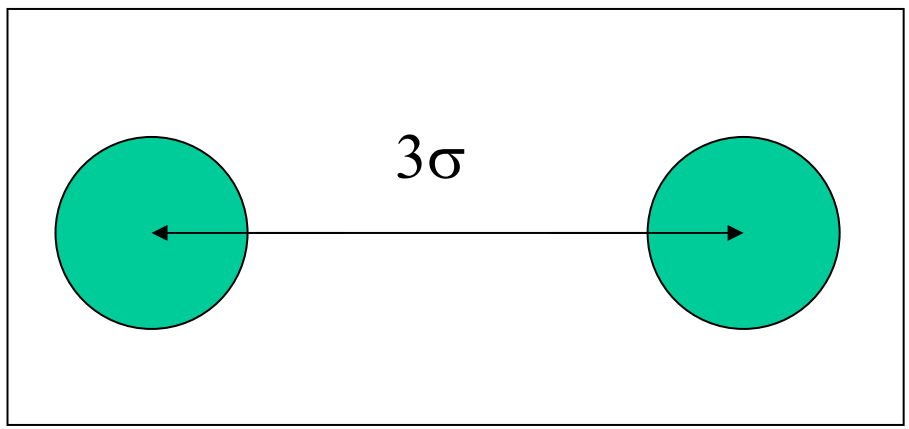
- Experimental observations
- Formulation of the theory
- Results in the colloid limit
- Comparison with experiments

Experimental observations of phase transitions in dispersions of highly charged colloids

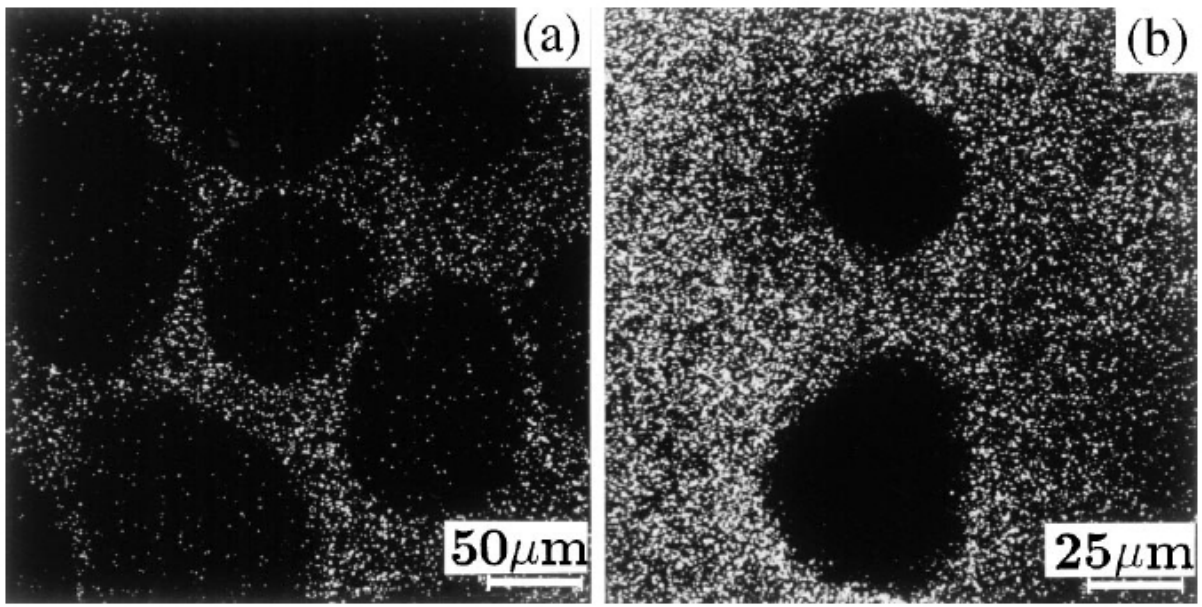
bcc crystal with a large unit cell (a~3σ) coexisting with 'voids' - gas-crystal transition



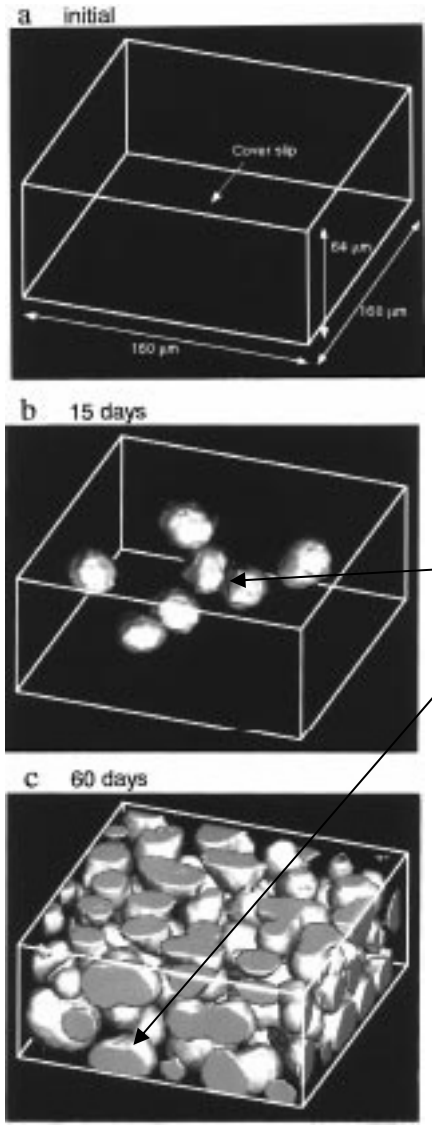


USAXS scattering profile indicates the bcc structure

CLSM micrographs. Dark regions represent voids.
σ=0.2μm, charge dens. 0.25 $\mu C/cm^2$, vol. frac.:
(a) ζ = 0.006, (b) ζ = 0.024,
Tata et. al. *Phys.Rev.Lett* **78,** 2660 (1997)



amorphous dense phase coexists with ‘voids’



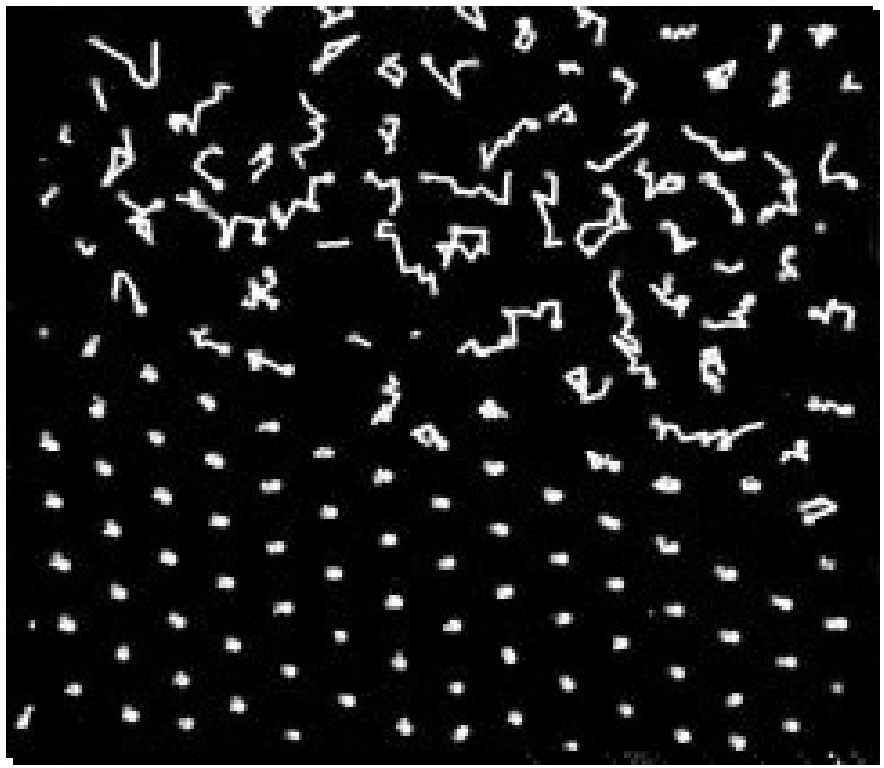
Time evolution of voids observed by confocal laser scanning microscope for latex particles σ=0.12 μm, vol.frac.=0.001

voids ~10 times larger than the average distance between particles

N.Ise et. al. JCP **78**, 536 (1983),
N.Ise et. al. Langmuir, **15**, 4176 (1999)

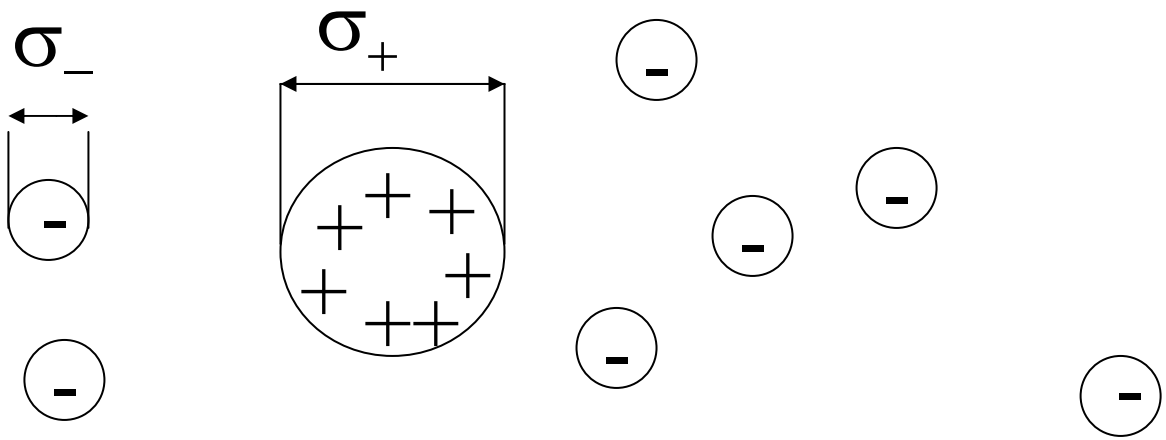
crystal-liquid coexistence

trajectories of the latex particles (Brownian motion), video imagery



σ=0.3 μm, vol. frac.= 0.02, charge dens.=1.3 μC/cm^2

Primitive model



Charge neutrality: $N_+ e_+ = N_- e_-$

$e_+ / |e_-| = Z$

$\sigma_+ / \sigma_- = \lambda$

$\sigma_{\alpha\beta} = (\sigma_\alpha + \sigma_\beta)/2$

$$V_{\alpha\beta}(r) = \frac{e_\alpha e_\beta \theta(r - \sigma_{\alpha\beta})}{Dr}$$

FIELD-THEORETIC APPROACH

Consider local densities of ionic species, $\rho_+(\mathbf{x})$ and $\rho_-(\mathbf{x})$

Probability of $\rho_+(\mathbf{x})$ and $\rho_-(\mathbf{x})$: $p \sim \exp(-\beta U[\rho_\alpha(\mathbf{x})])\, \mathcal{N}\, z$

$U[\rho_\alpha(\mathbf{x})]$ – system energy for given $\rho_\alpha(\mathbf{x})$,
$\mathcal{N} \sim \exp[\beta TS]$ – number of microscopic states compatible with $\rho_\alpha(\mathbf{x})$,
z – activity of ionic species.

$$p \sim \exp(-\beta \Omega^{MF} [\rho_\alpha(\mathbf{x})])$$

$\Omega^{MF} [\rho_\alpha(\mathbf{x})]$ -- grand thermodynamic potential for the local densities constrained to have the forms $\rho_+(\mathbf{x})$ and $\rho_-(\mathbf{x})$

FUNCTIONAL

$$\Omega^{MF}\left[\rho_\alpha(\mathbf{r})\right] = F_h\left[\rho_\alpha(\mathbf{r})\right] + U\left[\rho_\alpha(\mathbf{r})\right] - \mu_\alpha \int d\mathbf{r}\rho_\alpha(\mathbf{r})$$

The entropy is related to the free energy of the hard-sphere reference system by $F_h = -TS$

We assume that for all microstates compatible with $\rho_\alpha(\boldsymbol{r})$ the energy can be approximated by

$$U[\rho_\alpha(\boldsymbol{r})] = \frac{1}{2}\int d\boldsymbol{r}\int d\boldsymbol{r'}\ \rho_\alpha(\boldsymbol{r})V_{\alpha\beta}(\boldsymbol{r}-\boldsymbol{r'})\ \rho_\beta(\boldsymbol{r'})$$

MEAN-FIELD APPROXIMATION

Average densities

$$< \rho_\alpha (\mathbf{x})> = \Xi^{-1} \int D\, \rho_+ \int D\, \rho_- \, \rho_\alpha (\mathbf{x}) \exp(-\beta\, \Omega^{MF})$$

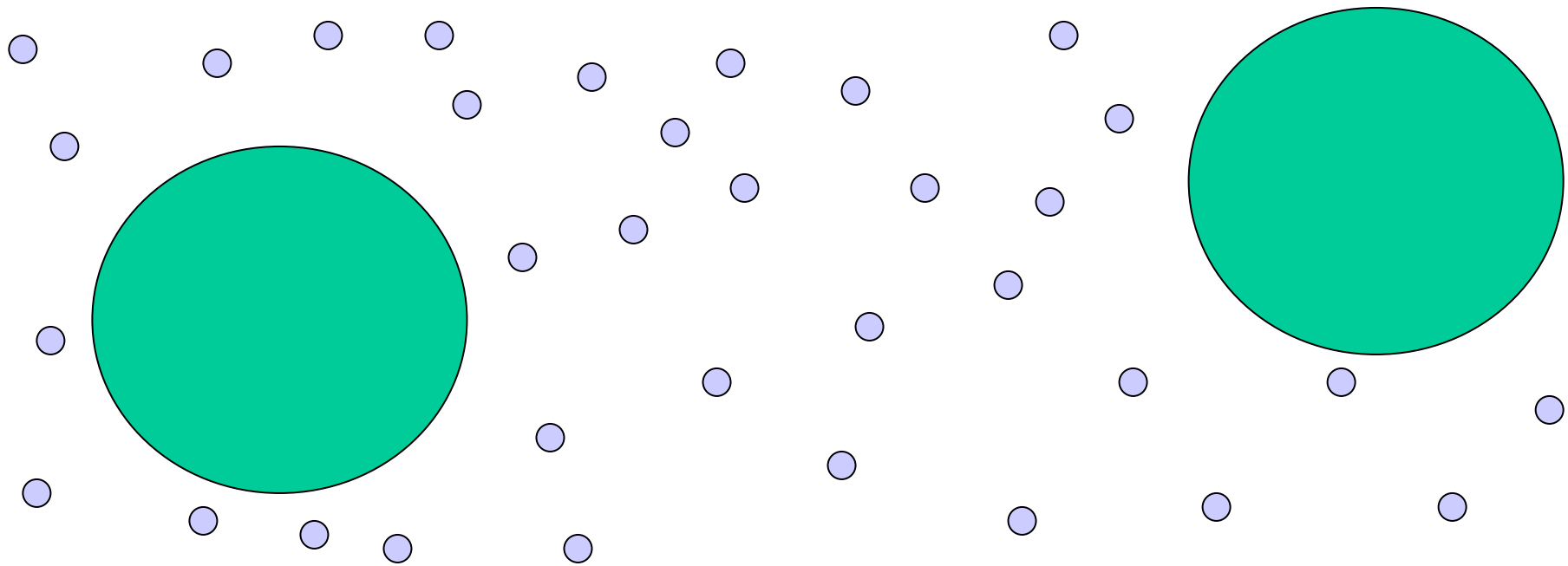
are approximated by their most probable values $\rho_{0\alpha} (\mathbf{x})$.

The grand potential Ω is approximated by $\Omega^{MF} [\, \rho_{0\alpha}(\mathbf{x})]$.

Colloid limit $\lambda, Z \longrightarrow \infty$ (with $Z/\lambda^3 \rightarrow 0$)

Thermodynamic variables: volume fraction ζ

inverse reduced temperature $\beta^* = \beta \dfrac{e_+ |e_-|}{D\sigma_{+-}}$



For small ζ the reference system is a mixture of ideal gases

Boundary of stability of the uniform dispersion

$$\Omega^{MF}=\Omega_0+\Omega_2+\Omega_{int}$$

$$\beta\,\Omega_2 = \frac{1}{2}\int_{\mathbf{k}}\Delta\,\tilde{\rho}_\alpha(-\mathbf{k})\,\tilde{C}_{\alpha\beta}(\mathbf{k})\,\Delta\,\tilde{\rho}_\beta(\mathbf{k})$$

where

$$\Delta\,\rho_\alpha = \rho_\alpha - \rho_{0\alpha} \qquad \tilde{C}_{\alpha\beta}(\mathbf{k}) = a_{\alpha\beta} + \beta\tilde{V}_{\alpha\beta}(\mathbf{k})$$

and

$$\beta\tilde{V}_{\alpha\beta}(\mathbf{k}) = 4\pi\beta^* \frac{e_\alpha e_\beta \cos(k\,\sigma_{\alpha\beta}/\sigma_{+-})}{e_+ e_-\ k^2}$$

$$\det \tilde{C}_{\alpha\beta}(\mathbf{k}) = 0 = \frac{d\,[\det \tilde{C}_{\alpha\beta}(\mathbf{k})]}{d\ k}$$

Boundary of stability of the uniform phase –
no minimum of Ω^{MF} for uniform densities.

In the colloid limit we find that the periodic structure

$\Delta\rho_+(\mathbf{r}) \sim \cos(\mathbf{r} \cdot \mathbf{k}_b)$ with $k_b = 2.46\sigma^{-1}$

is more stable than the uniform dispersion for

$$T^* < 1.55 Z\, \zeta$$

Order of the phase transition and structure of the ordered phase

After rescaling the potential and the field we obtain

$$\beta\Omega[\psi]=\frac{1}{2}\int_{\mathbf{k}}\tilde{\psi}(\mathbf{k})\tilde{C}_p(\mathbf{k})\tilde{\psi}(-\mathbf{k}) + \\ - \frac{a_3}{3!}\int_{\mathbf{r}}\psi^3(\mathbf{r}) + \frac{a_4}{4!}\int_{\mathbf{r}}\psi^4(\mathbf{r})$$

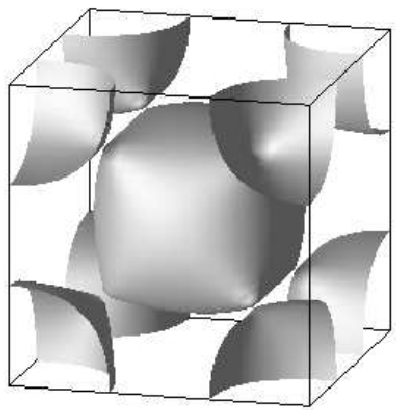
A functional of the same form was studied by L.Leibler in the case of block copolymers. First-order transition to the bcc crystal.

$$T^*=1.64\ Z\ \zeta$$

lattice constant = 3.6 σ

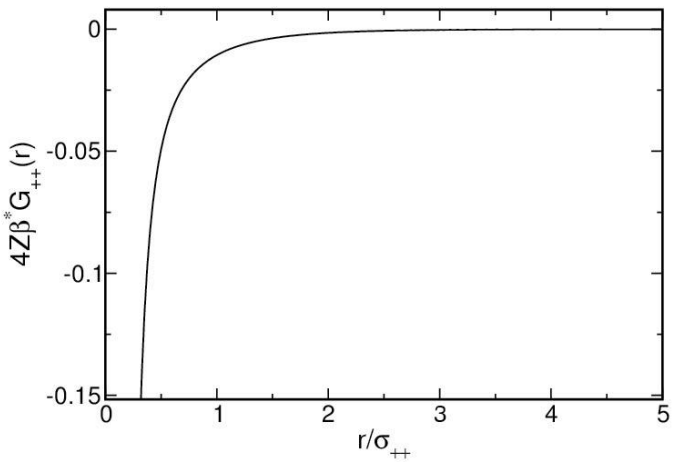
Unit cell of the ordered structure

Surface separating the region of excess density of particles (inside) from the region of depleted density in the unit cell of the bcc crystal. Lattice constant is $a = 3.6\sigma$.

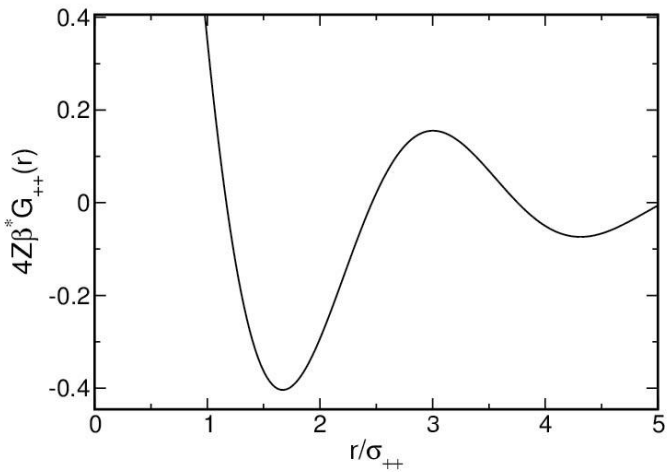


Particle-density correlation function in the gas phase

Far from the phase coexistence



At the phase coexistence



Comparison with experiments

bcc crystal -- agreement

lattice constant 3.6σ -- good agreement

density of the gas phase at the coexistence with the bcc:

for typical experimental values $Z \sim 10^3$-10^5, $\lambda \sim 10^3$
we find $\zeta = 10^{-4}$-10^{-8} -- strong dilution, agreement with 'voids' observed in experiments

SUMMARY

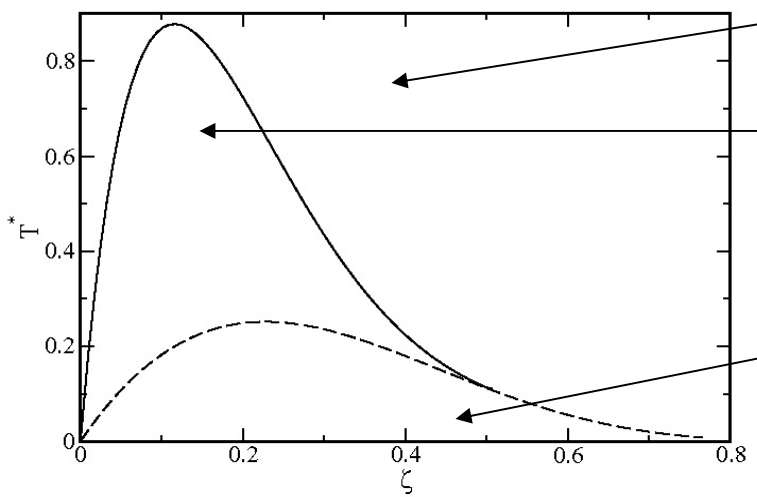
- The model can describe ionic systems with arbitrary size- and charge- asymmetries.

- The RPM model (ordinary electrolytes), the colloidal systems and the whole crossover region can be described within the same approach

- The role of fluctuations can be determined in the future work

SPINODALS AND THE CRITICAL WAVEVECTOR BEYOND THE COLLOID LIMIT

$Z=\lambda=12$

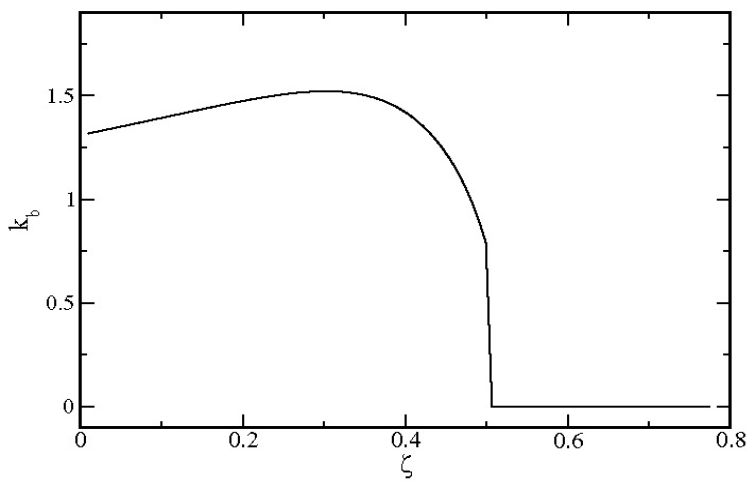


uniform

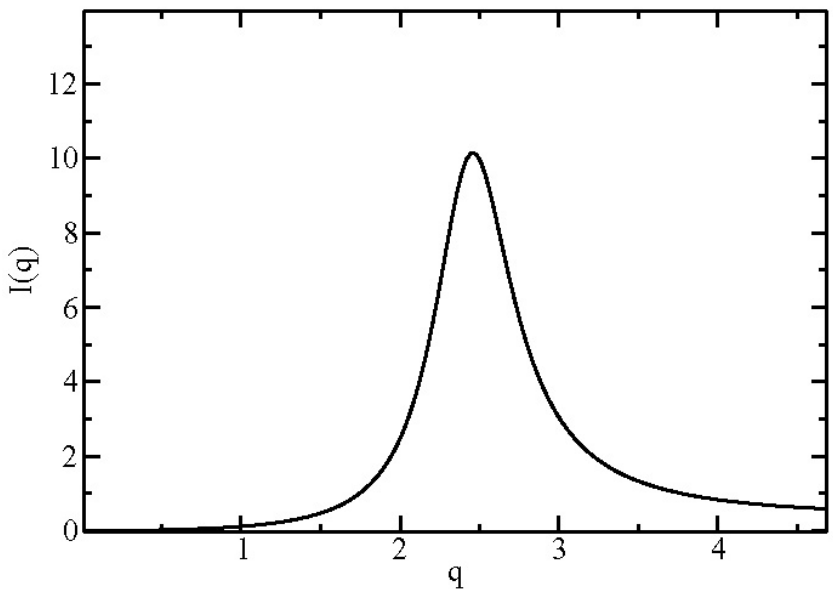
crystal, k_b

phase-separated, $k_b=0$

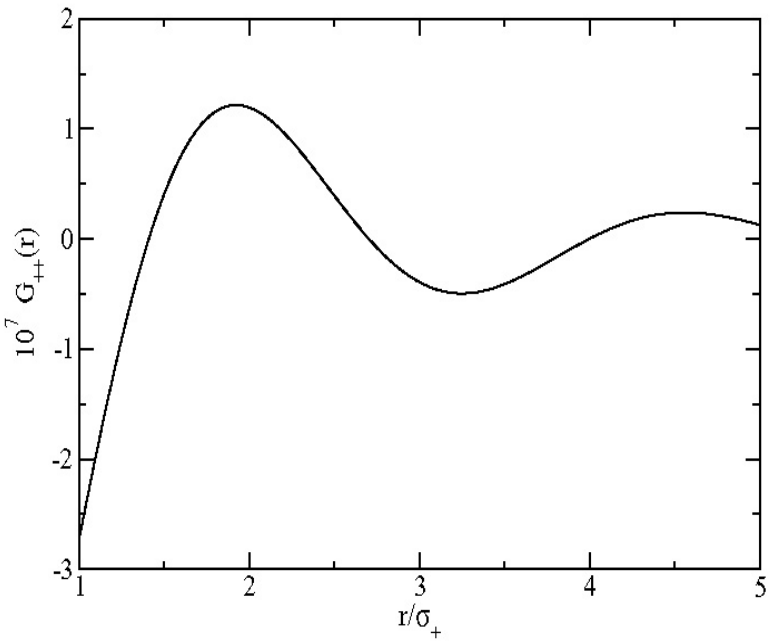
Reentrant phase transition



Structure factor in the gas phase at the coexistence with the bcc crystal



Oscillatory decay of the correlation function in real space,
effective attractions for $r \sim 2\sigma$



$$\tilde{V}_{++}(k) \sim \frac{\cos(2k)}{k^2}$$