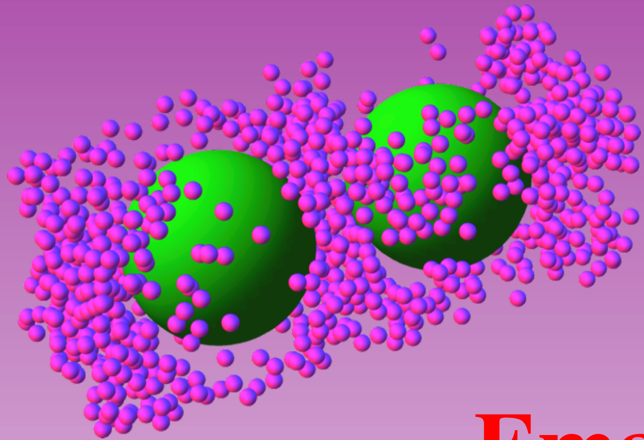
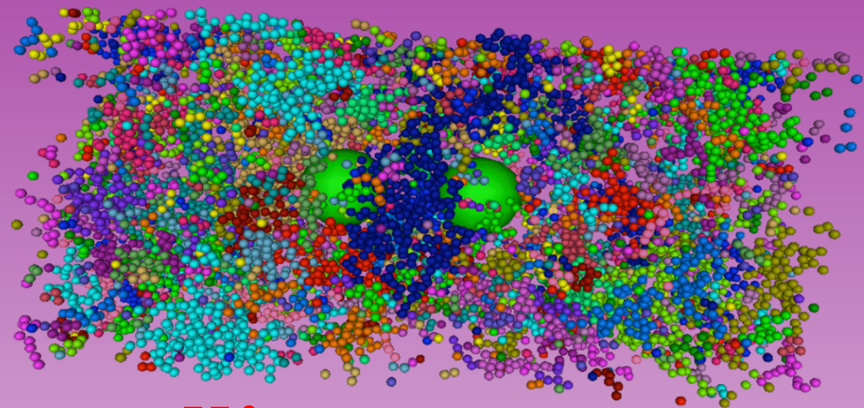
Tuning colloidal interactions by controlling the solvent properties: critical Casimir forces and beyond





Emanuela Zaccarelli

Nicoletta Gnan and Francesco Sciortino

institute for complex systems

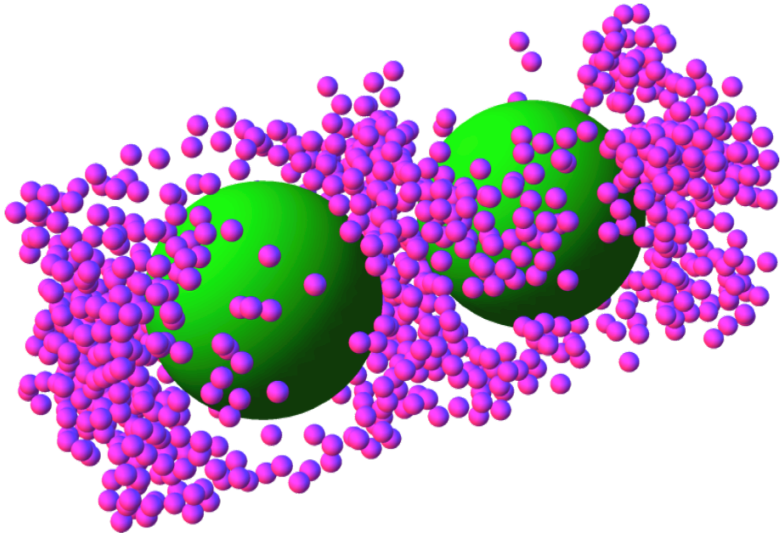
SAPIENZA UNIVERSITÀ DI ROMA

FUTURO IN RICERCA

Flowing matter across the scales

Rome, 26th March 2015

Introduction



Specific interactions between colloids allow to explore new phases and states

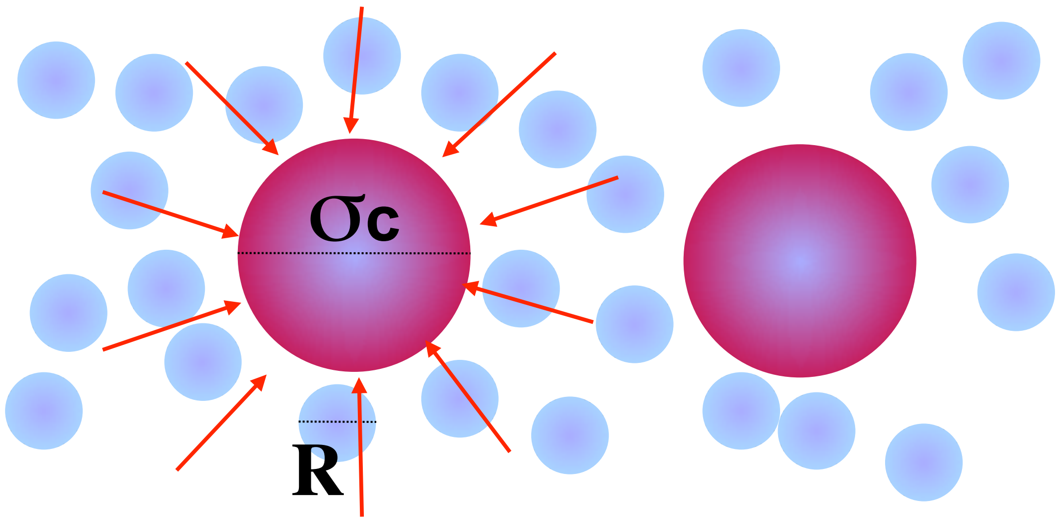
The addition of co-solute particles allows to manipulate and control the phase behaviour of colloids by means of effective interactions, e.g. depletion

Co-solute properties can be exploited, to create new types of effective interactions among colloids

When co-solute particles are much smaller than colloids, an analogy can be drawn with interactions induced by a molecular solvent:
can depletion be related to critical Casimir effect?

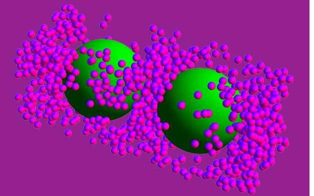
Introduction: Depletion Interactions

Colloids in solution with depletant particles

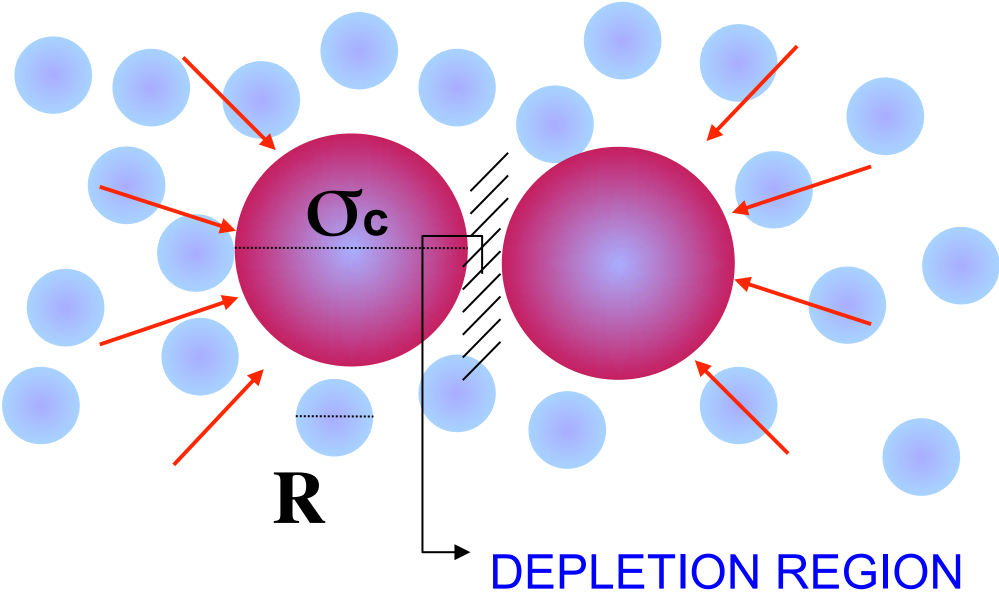


When the two colloids are at distances larger than *2R* the net pressure on each colloid is zero

Introduction: Depletion Interactions



Colloids in solution with depletant particles

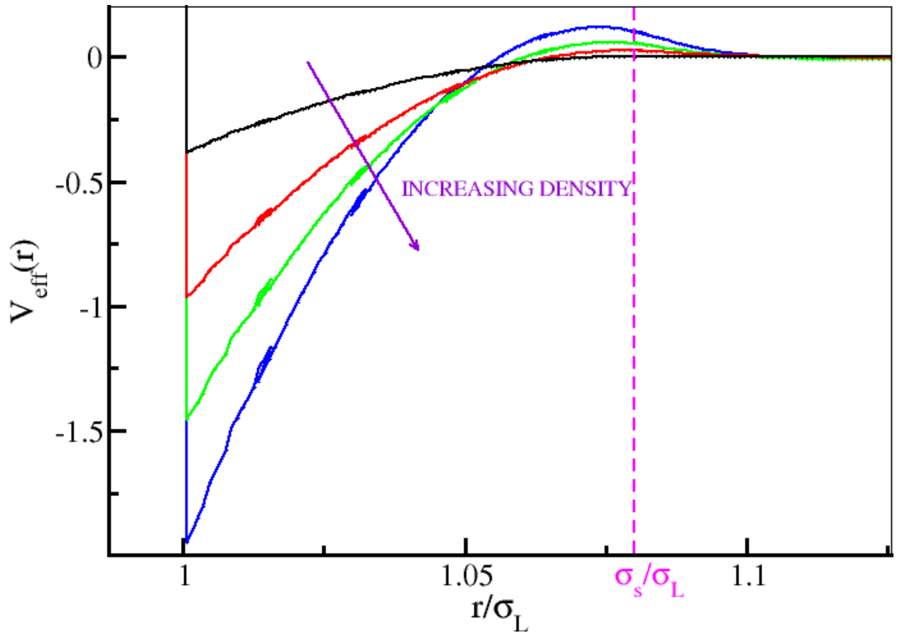


When the two colloids are closer than *2R* a "depletion" region appears. The mismatch of the pressure inside and outside the colloids give rise to an effective attraction

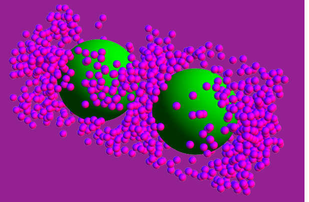
- Entropy-driven interactions

-The **range** is controlled by the **size** of depletant

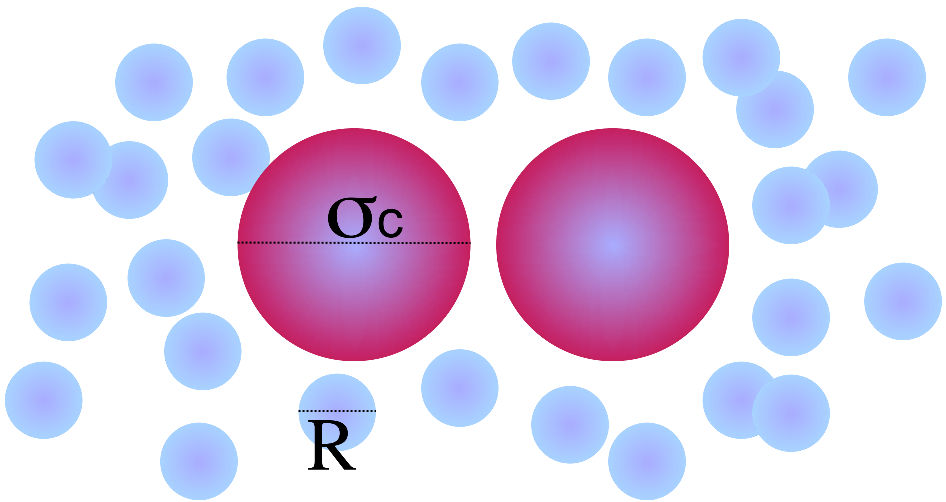
-The **strength** is controlled by the **concentration** of depletant



Introduction: Depletion Interactions



Colloids in solution with depletant particles



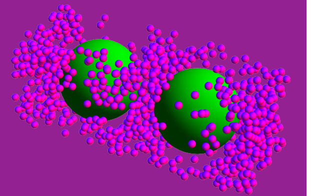
The depletion force can be calculated analytically in the famous **Asakura-Oosawa** model: *hard-sphere colloids with ideal depletant* (hard-core interactions between colloid and depletant particles)

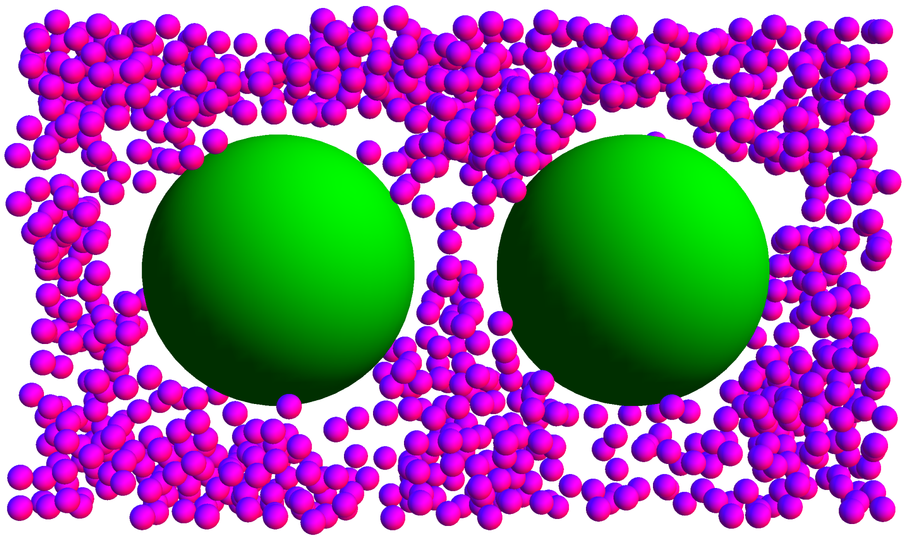
$$\beta V_{AO}(r,R,\rho) = -\pi\rho\,(2R-r)\left[\left(\frac{R\sigma_c}{2}+\frac{2R^2}{3}\right) - \frac{r}{2}\left(\frac{\sigma_c}{2}+\frac{R}{3}\right) - \frac{r^2}{12}\right]\Theta(2R-r)$$

R radius of the depletant
r colloids surface-to-surface distance
ρ density of the depletant

Θ-function indicates that the potential vanishes for distance longer than 2R

Tuning effective interactions by a solvent: Critical Casimir Forces





Consider a non-ideal depletant:

a very interesting situation arises when the solvent (or depletant) is close to criticality

The confinement of the critical fluctuations* of the order parameter close to the critical point gives rise to an effective force between the colloids

M. E. Fisher and P. G. deGennes, C. R. Acad. Sci. Paris B287,209 (1978)

*** in analogy with the Casimir effect**

Casimir effect

- confinement of quantum fluctuations of magnetic field in vacuum

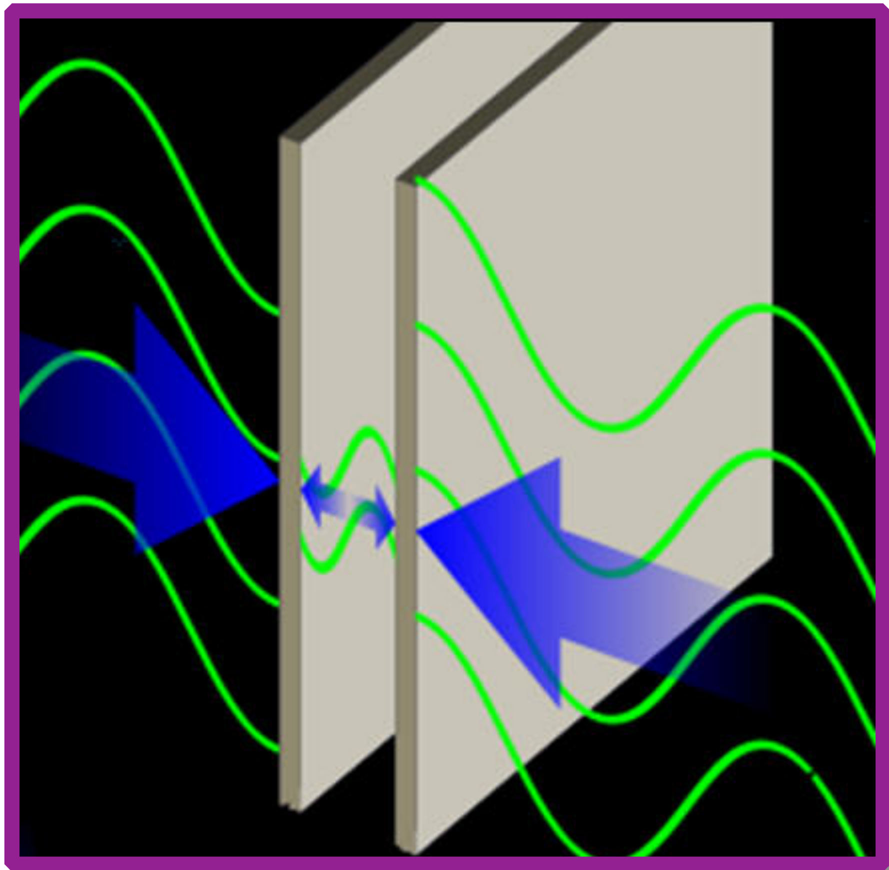
Outside the plates: no restrictions

Inside the plates: only the mode having a node at the plate surfaces are allowed

Net pressure of the total field outside the two plates

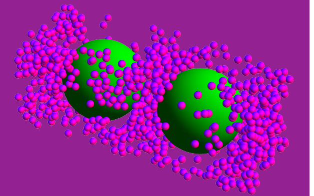
$$F_{\mathrm{Cas}} = \frac{\hbar c \pi^2 A}{240 L^4}$$

Neutral conducting metallic plates



H. B. G. Casimir, Proc. Kon. Nederl. Akad. Wet. B51,793 (1948)

Critical Casimir Forces: Theoretical results



The critical Casimir force depends on

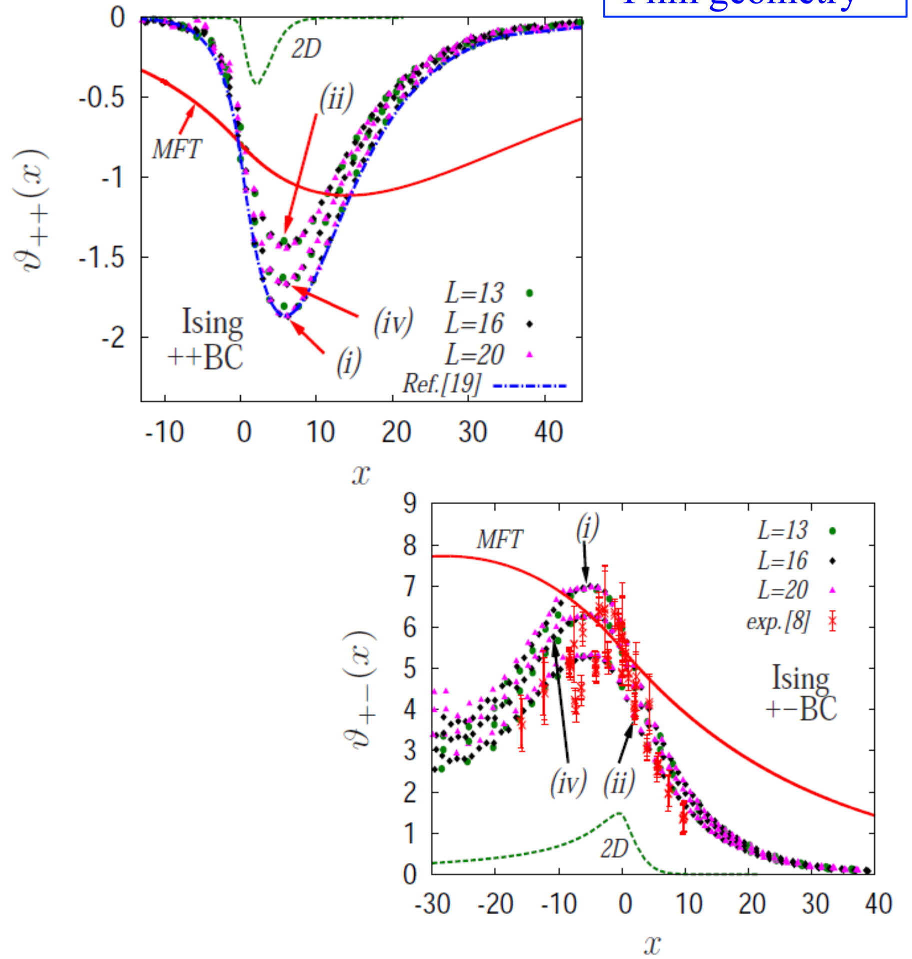
- The distance between the confining surfaces
- The geometry of the confining surfaces
- The ability of the confining surfaces to absorb or not the confined medium (Boundary Conditions)

Universal scaling function between two spheres

$$\beta\Phi(z) = \frac{\sigma_c}{z}\Theta(z/\xi)$$

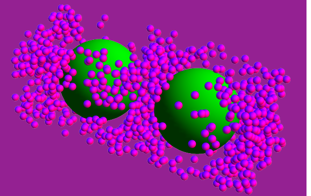
$$\Theta(z/\xi)_{(\pm,\pm)}(z/\xi \gg 1) = \pi A_{(\pm,\pm)}(z/\xi)e^{-(z/\xi)}$$

Film geometry



O. Vasilyev, A. Gambassi, A. Maciolek and S. Dietrich. *PRE* **79**, (2008).

Critical Casimir Forces: Experimental results



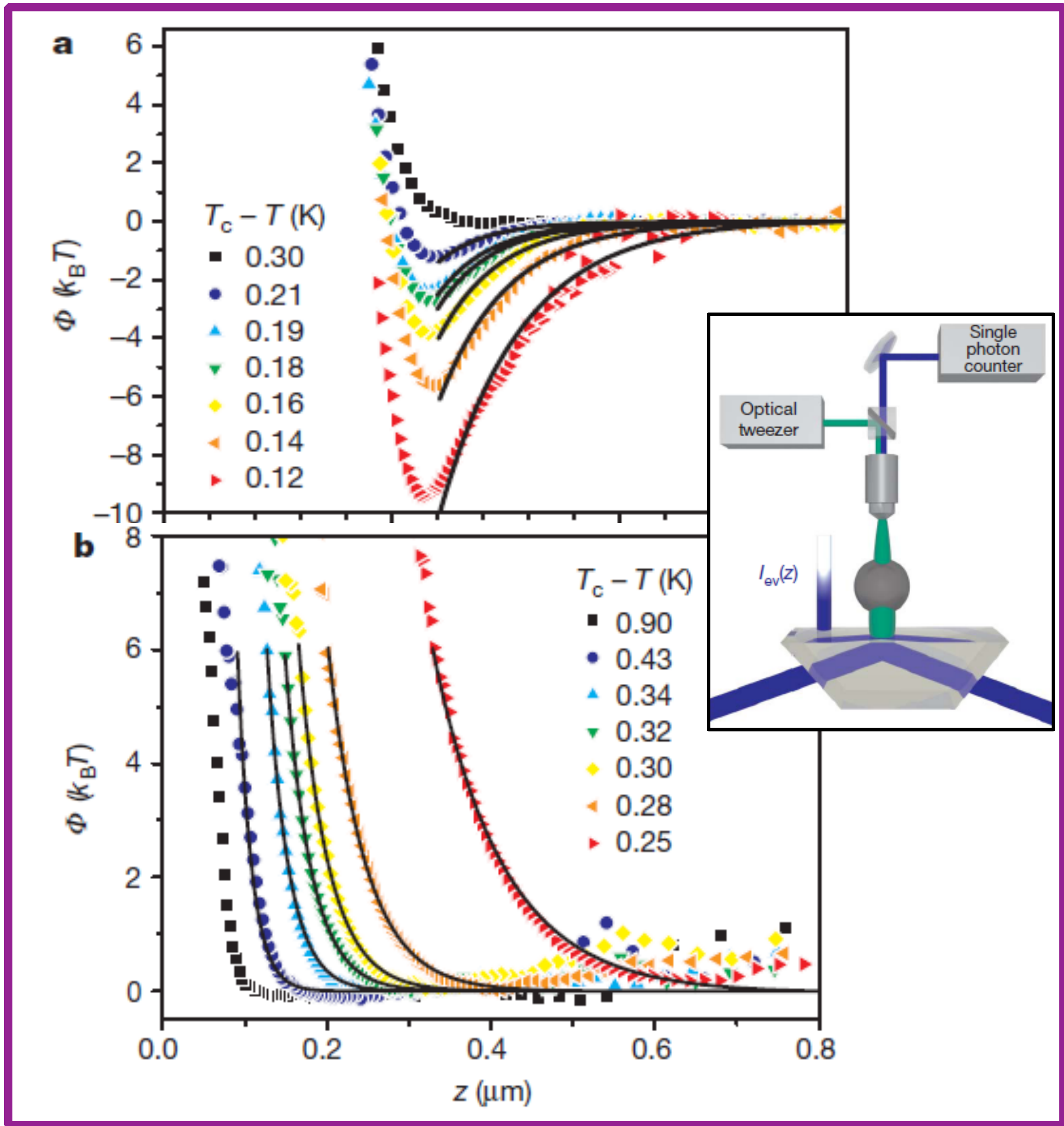
Direct experimental measurements and verification of the universal scaling form

$$\beta\Phi(z) = \frac{\sigma_c}{z}\Theta(z/\xi)$$

$$\Theta(z/\xi)_{(\pm,\pm)}(z/\xi \gg 1) = \pi A_{(\pm,\pm)}(z/\xi)e^{-(z/\xi)}$$

The range can be controlled by finely tuning the solvent temperature close to the critical point

The sign depends on the adsorption properties of the confining surfaces towards the confined medium

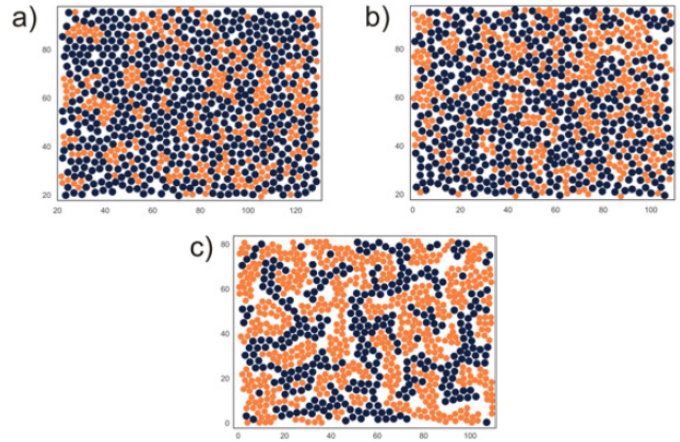


C. Hertlein, L. Helden, A. Gambassi, S. Dietrich & C. Bechinger. *Nature* **451** (2008)

Critical Casimir Forces: Experimental results

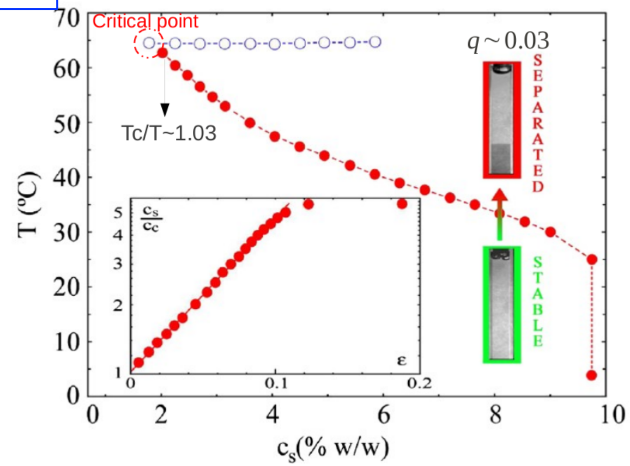
- Critical Casimir forces can induce colloidal aggregation

Molecular solvent



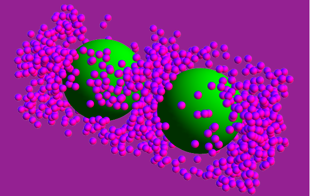
O. Zvyagolskaya, A. J. Archer and C. Bechinger. *EPL* **96** (2011)

Depletant

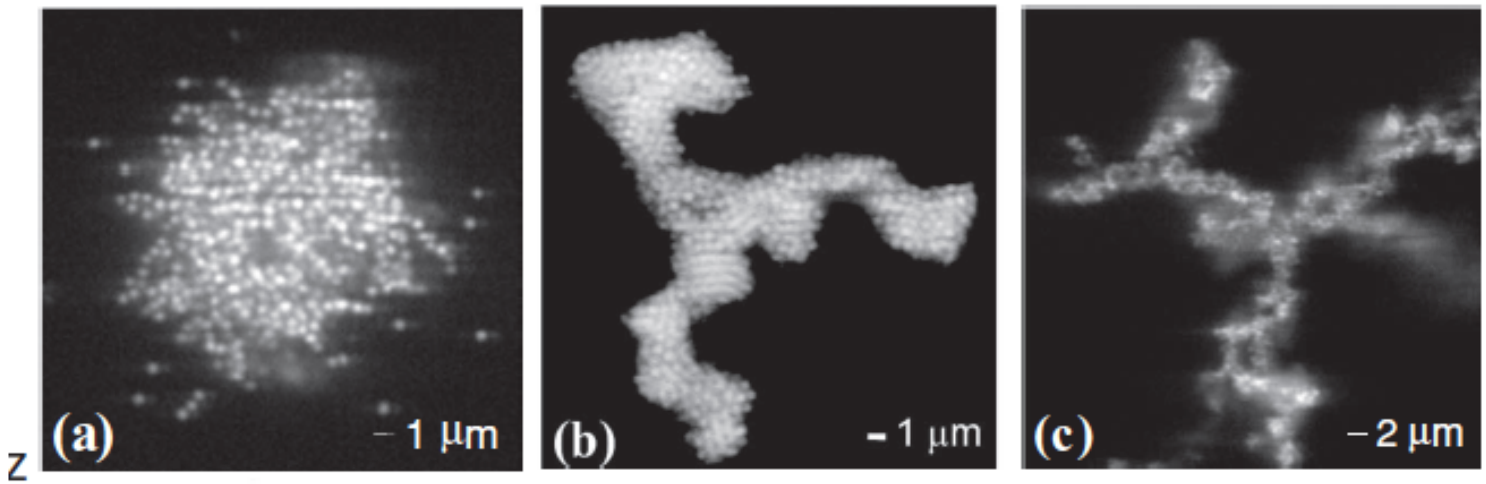


S. Buzzaccaro, J. Colombo, A. Parola, and R. Piazza. *PRL* **105**, (2010)

Critical Casimir Forces can be exploited to control colloidal aggregation

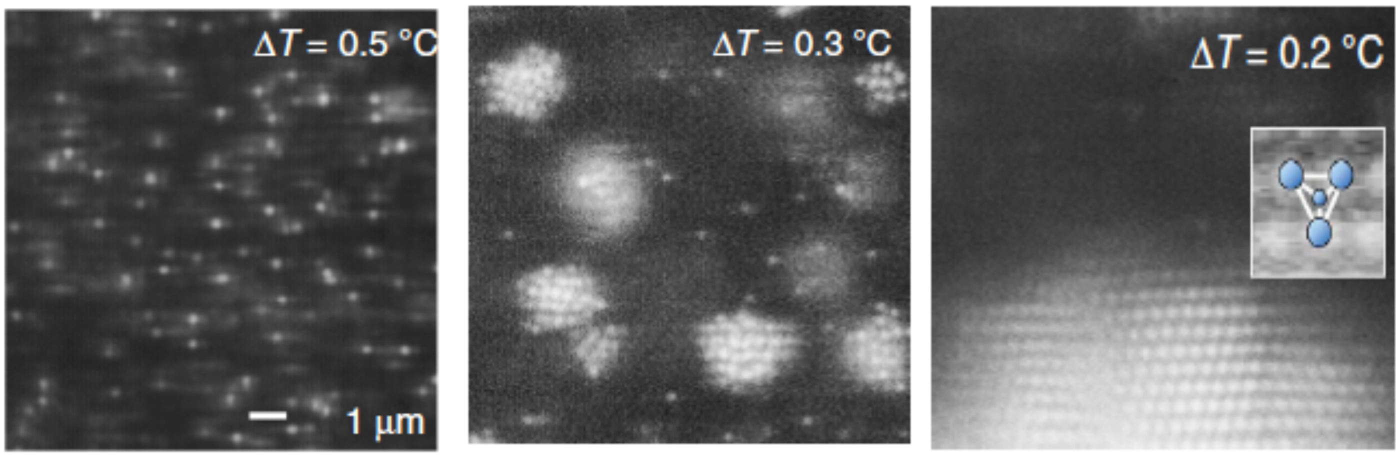


Colloids in a Molecular solvent



changing
ΔT

P.B. Shelpe, V. D. Nguyen. A. V. Limaye and P. Schall Adv. Mater. 25, 1499 (2013)



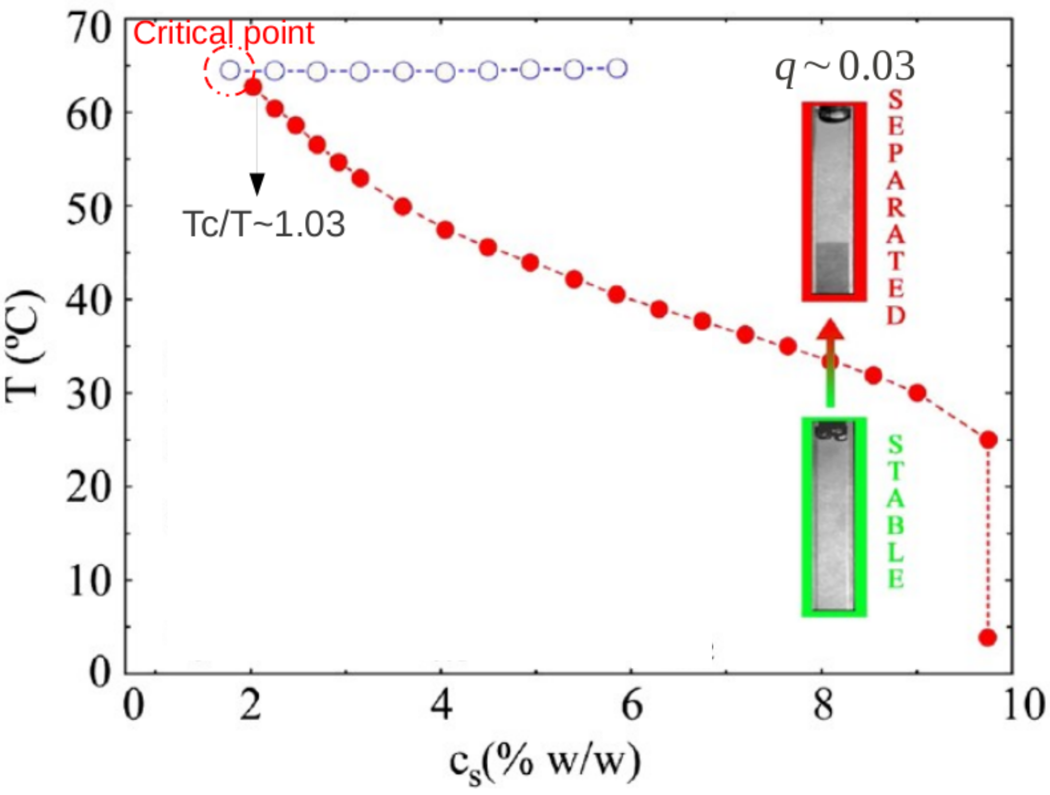
V. D. Nguyen, S. Faber, Z. Hu, G. H. Wegdam and P. Schall, Nature Commun. 4, 1584 (2013)

When depletion goes critical

Depletant: non ionic micelles with a critical point at high T

- A **continous line** can be drawn **separating** the region where **colloids** are **stable** from the region where **colloids aggregate.**

Colloids in a Depletant



S.Buzzaccaro, J. Colombo, A. Parola, and R. Piazza. *PRL* **105**, (2010);
R. Piazza et al J. Phys.: Condens. Matter 23,194114 (2011).

When depletion goes critical

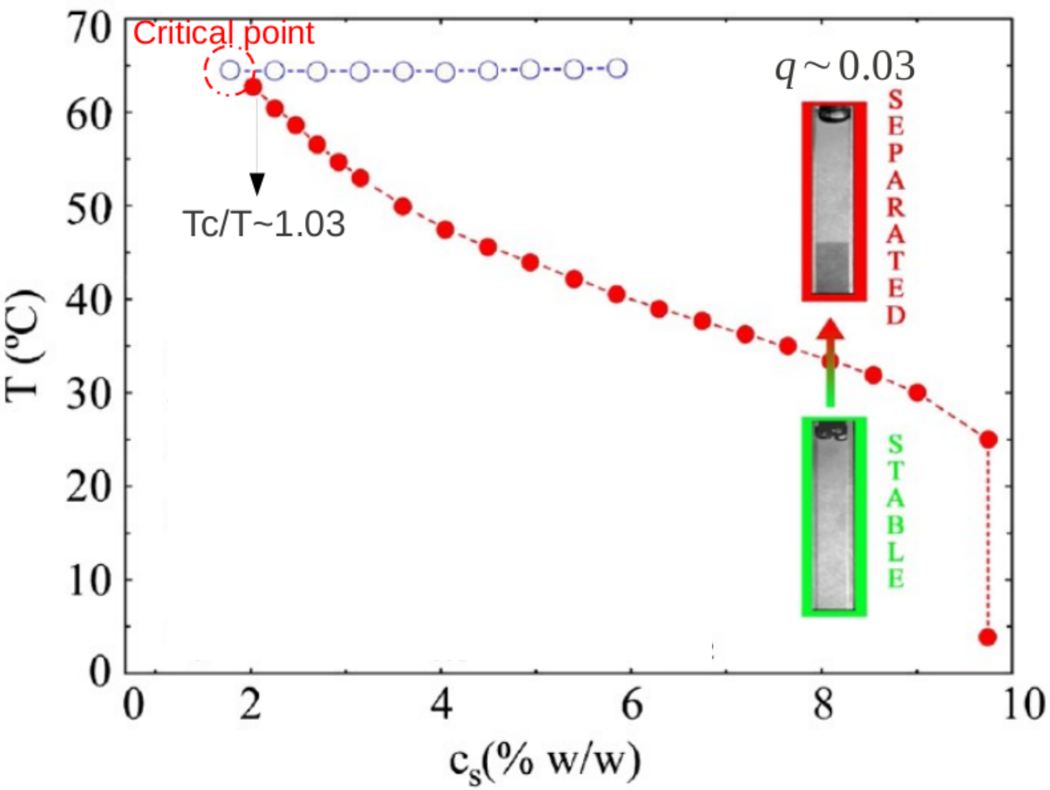
Depletant: non ionic micelles with a critical point at high T

- A **continous line** can be drawn **separating** the region where **colloids** are **stable** from the region where **colloids aggregate.**

- **Far from the critical point** colloidal reversible aggregation occurs due to **depletion effect**

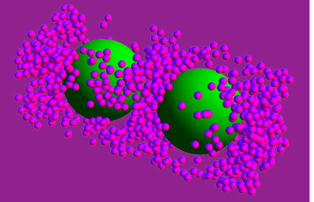
- **Close to the critical point critical Casimir forces** are observed and represent the dominant contribution in the effective potential

Colloids in a Depletant



S.Buzzaccaro, J. Colombo, A. Parola, and R. Piazza. *PRL* **105**, (2010);
R. Piazza et al J. Phys.: Condens. Matter 23,194114 (2011).

Do critical fluctuations play a role in colloidal phase separation? An answer from simulations

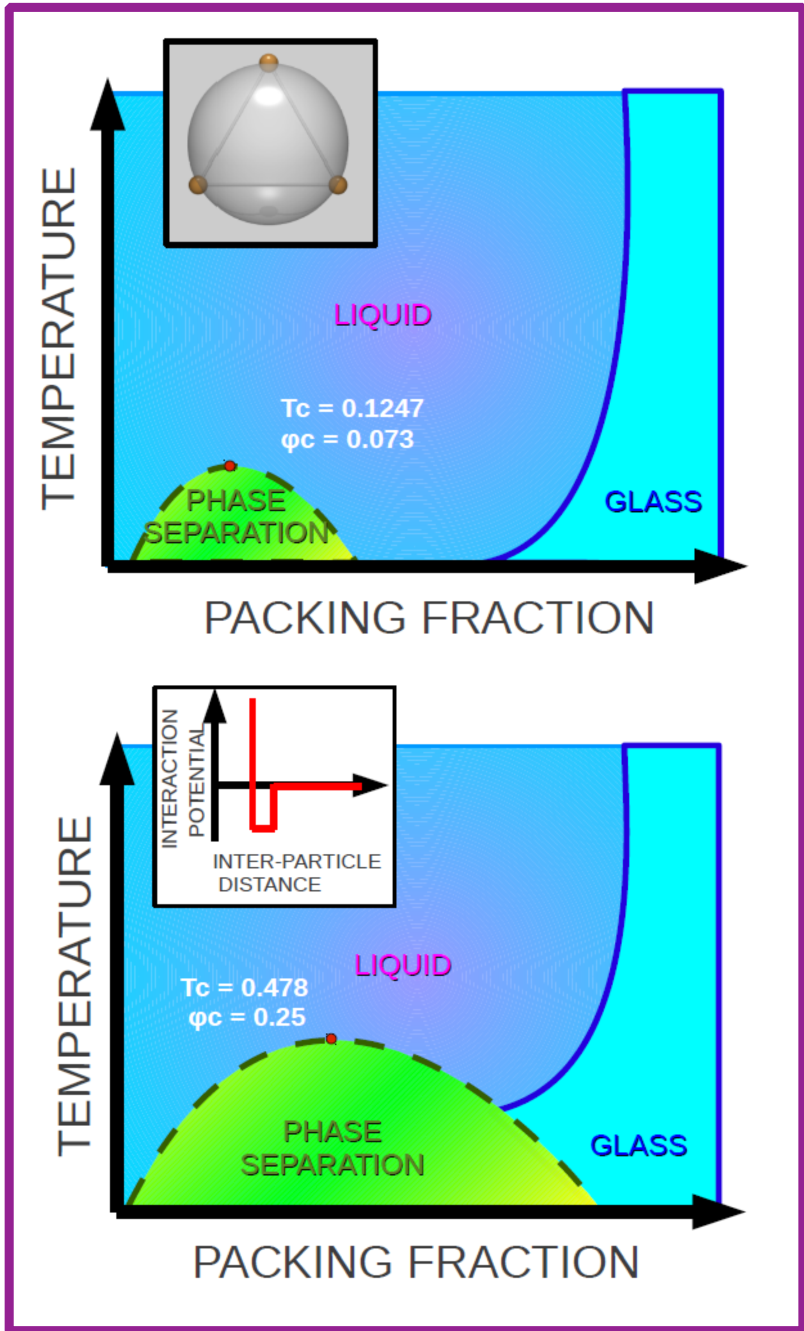


Two depletant models have been considered:

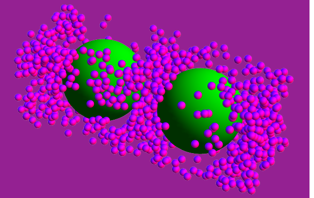
- a **three-patch model** (3P) with a **low-density critical point** to reproduce the experiment of S. Buzzaccaro *et al.*

- an isotropic **square-well attraction (SW)**

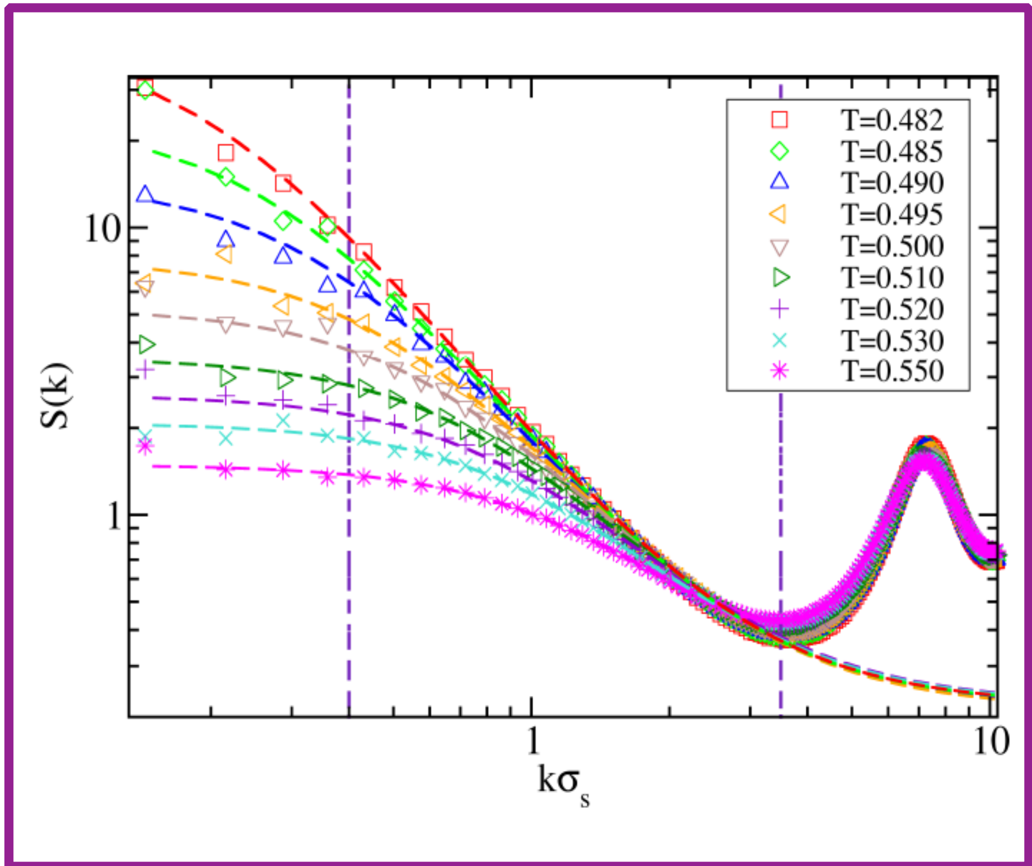
The effective force acting on two hard-sphere colloids is evaluated through umbrella sampling Monte Carlo simulations.

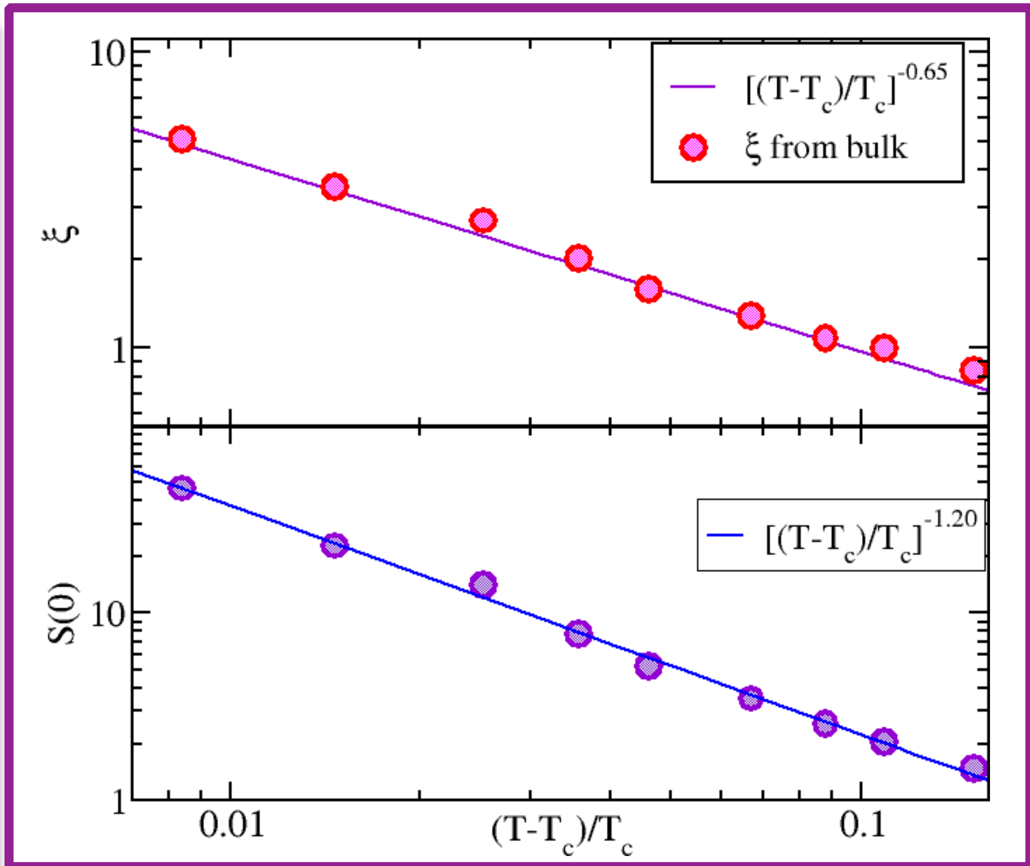


Critical behavior of the depletant



- We determine the thermal correlation length ξ in the bulk SW system



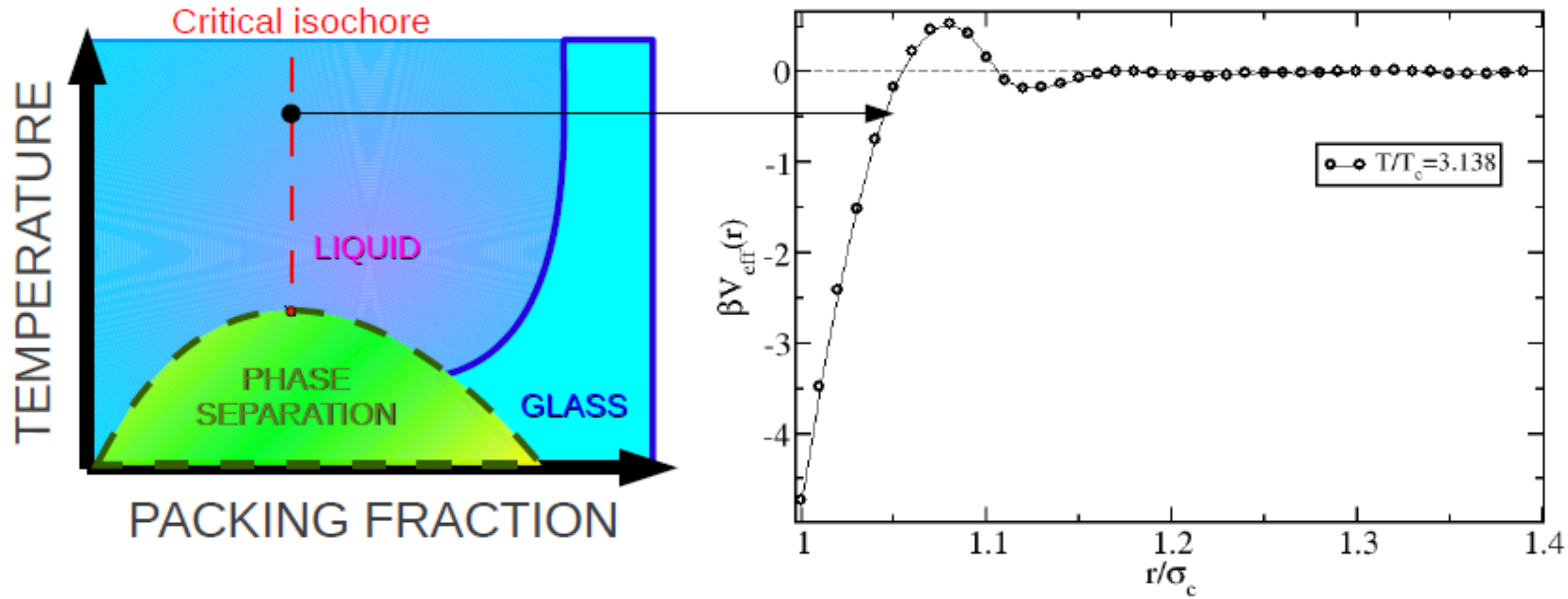


$$S(k) = c + \frac{S(0) - c}{1 + \xi^2 k^2}$$

Results: Effective potentials of hard-sphere colloids in a depletant approaching the critical point

- For **T >> Tc** a typical depletion potential for a hard-sphere depletant is observed. The range of attraction is set by the radius of the depletant

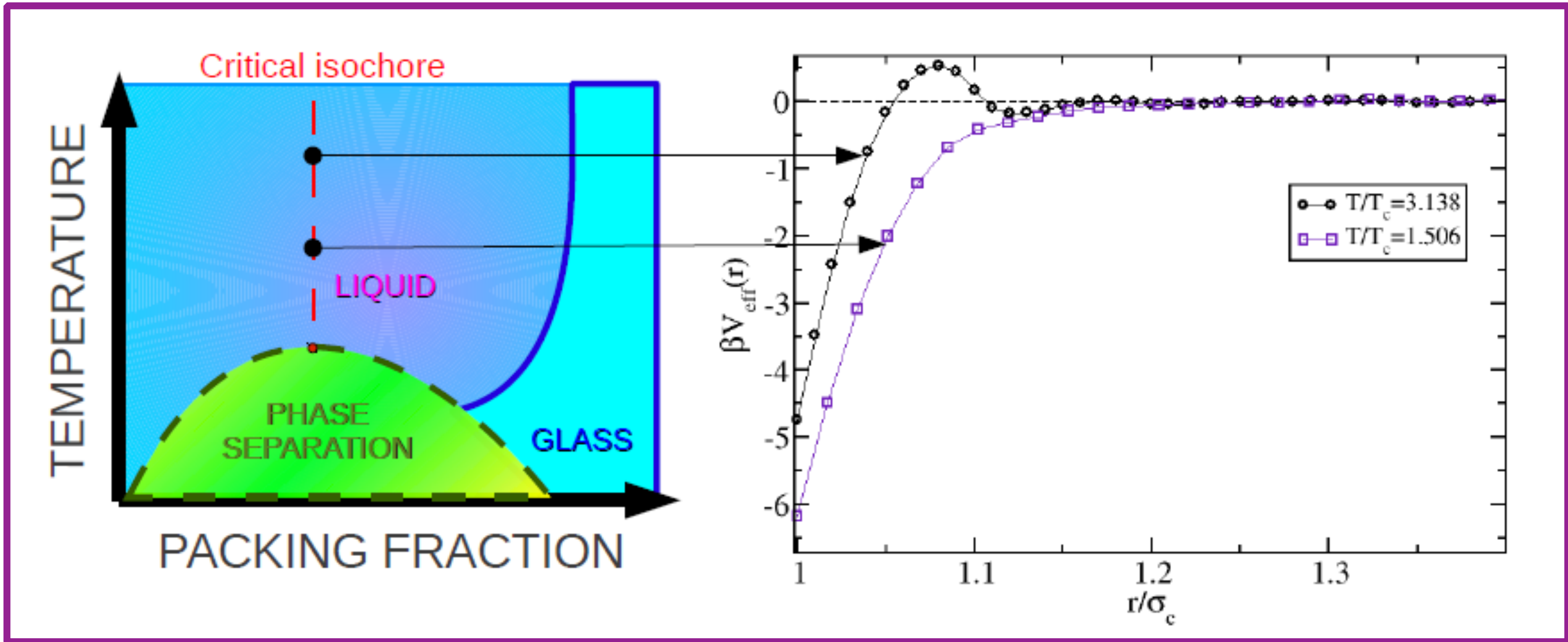
(in this case 0.1σc)



N. Gnan, EZ, P. Tartaglia and F. Sciortino *Soft Matter 8, 1991 (2012)*

Results: Effective potentials of hard-sphere colloids in a depletant approaching the critical point

- **Decreasing T** V*eff* loses its oscillatory character and turns into a **completely attractive** potential



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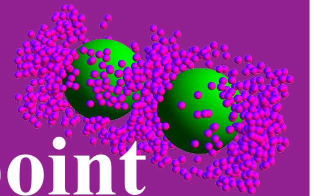
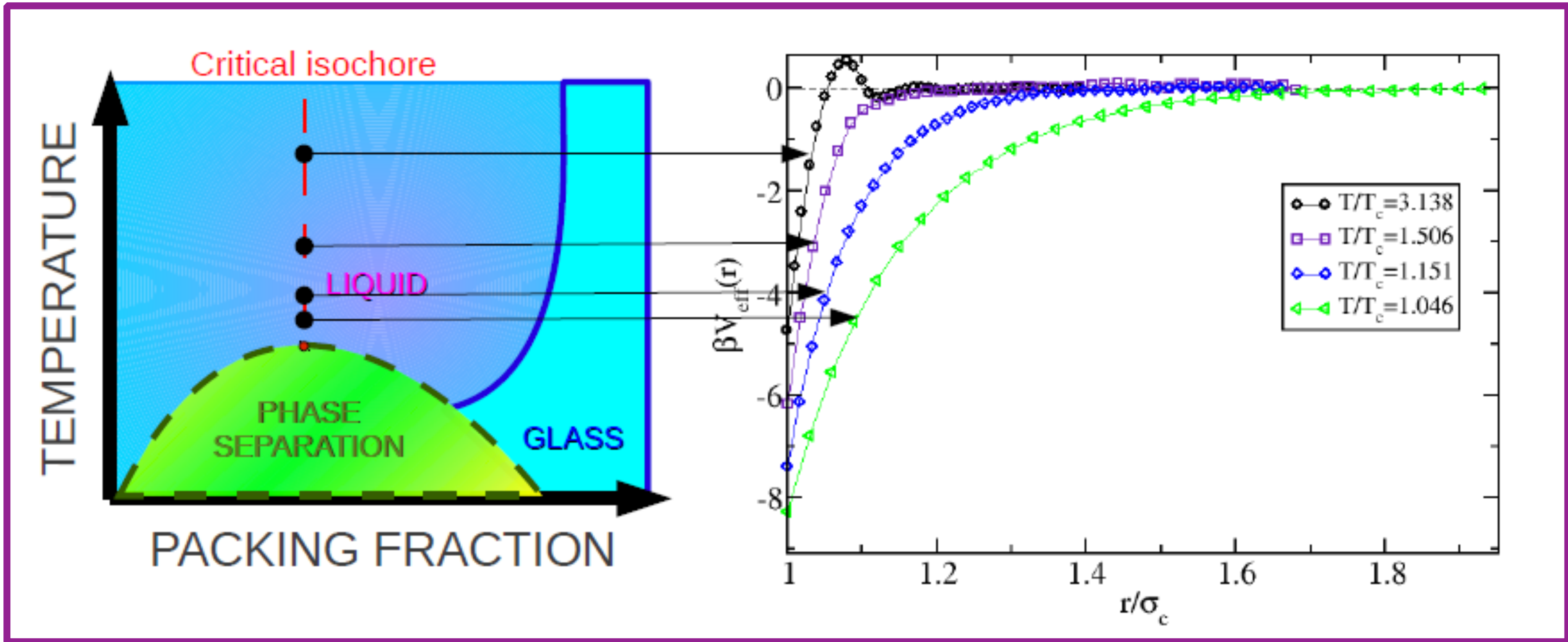


- A progressive significant **increase of the interaction range** is observed **on approaching Tc**



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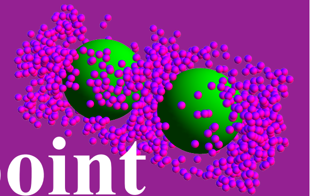
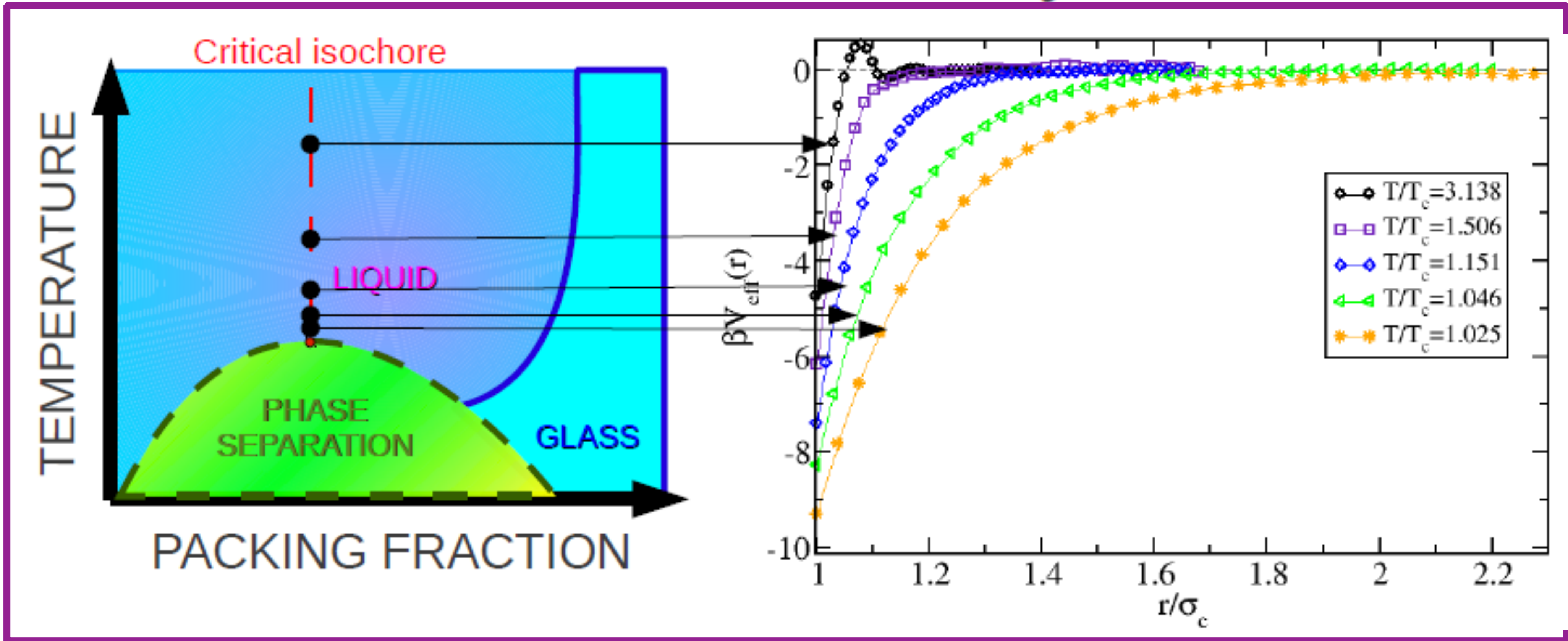


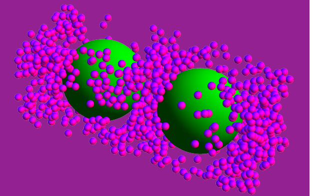
In the "sphere-sphere" geometry the long distance behavior of the critical Casimir potential is

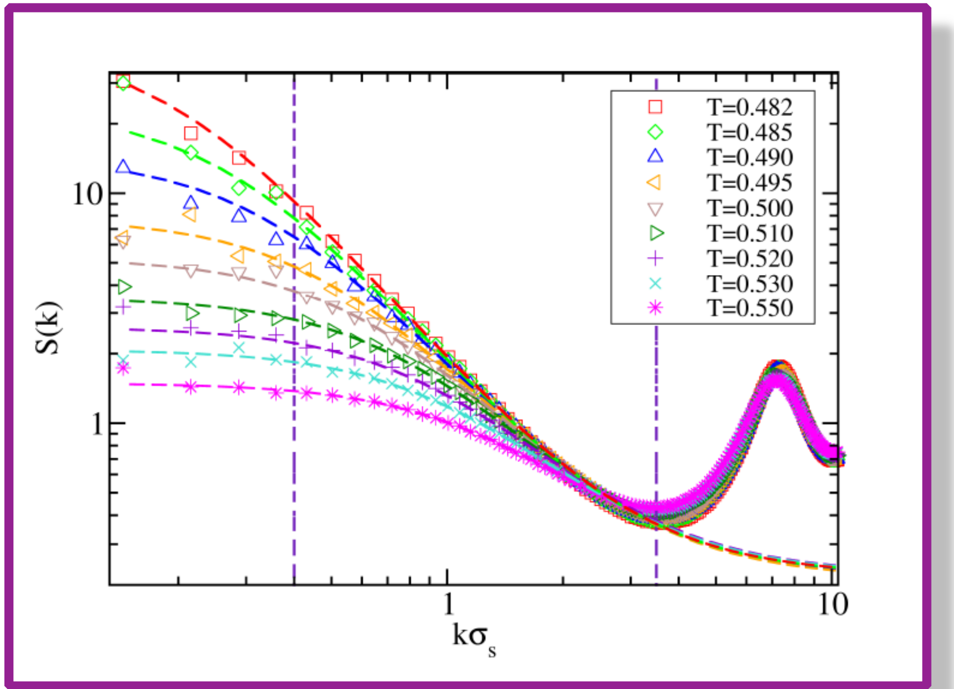
$$\beta\Phi(r) = \pi A \frac{\sigma_c}{\xi} e^{-(r-\sigma_c)/\xi}$$



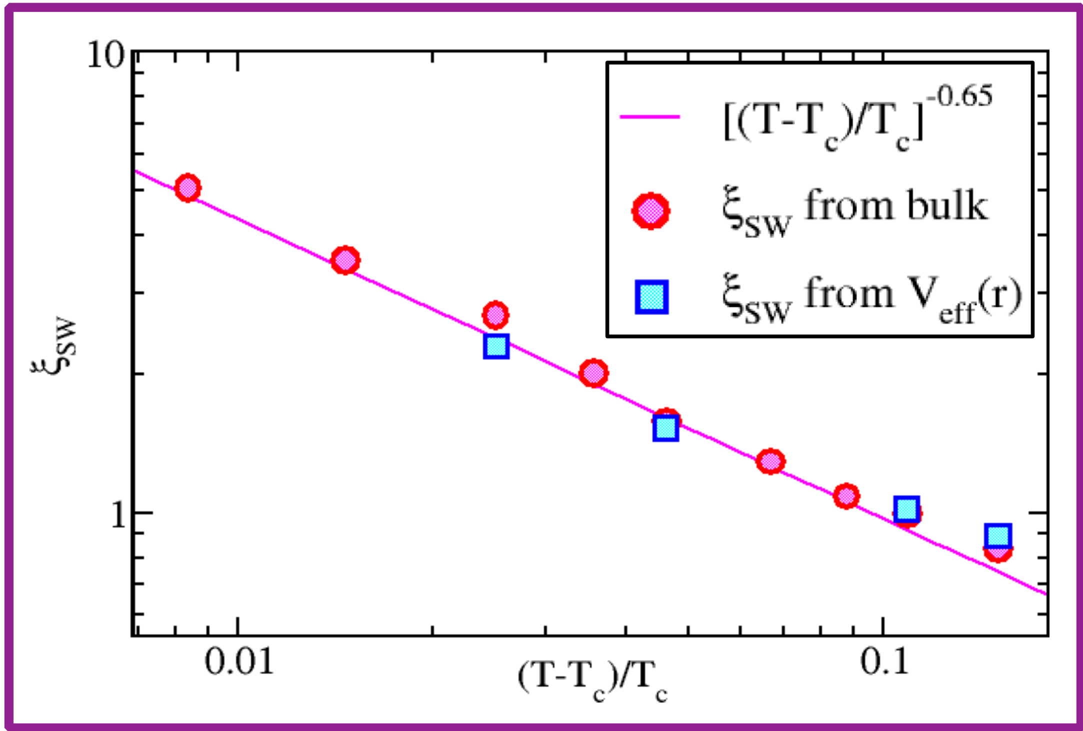
N. Gnan, EZ, P. Tartaglia and F. Sciortino *Soft Matter 8, 1991 (2012)*

Results: correlation length





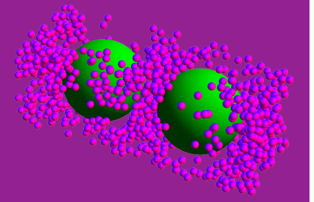
$$S(k) = c + \frac{S(0) - c}{1 + \xi^2 k^2}$$



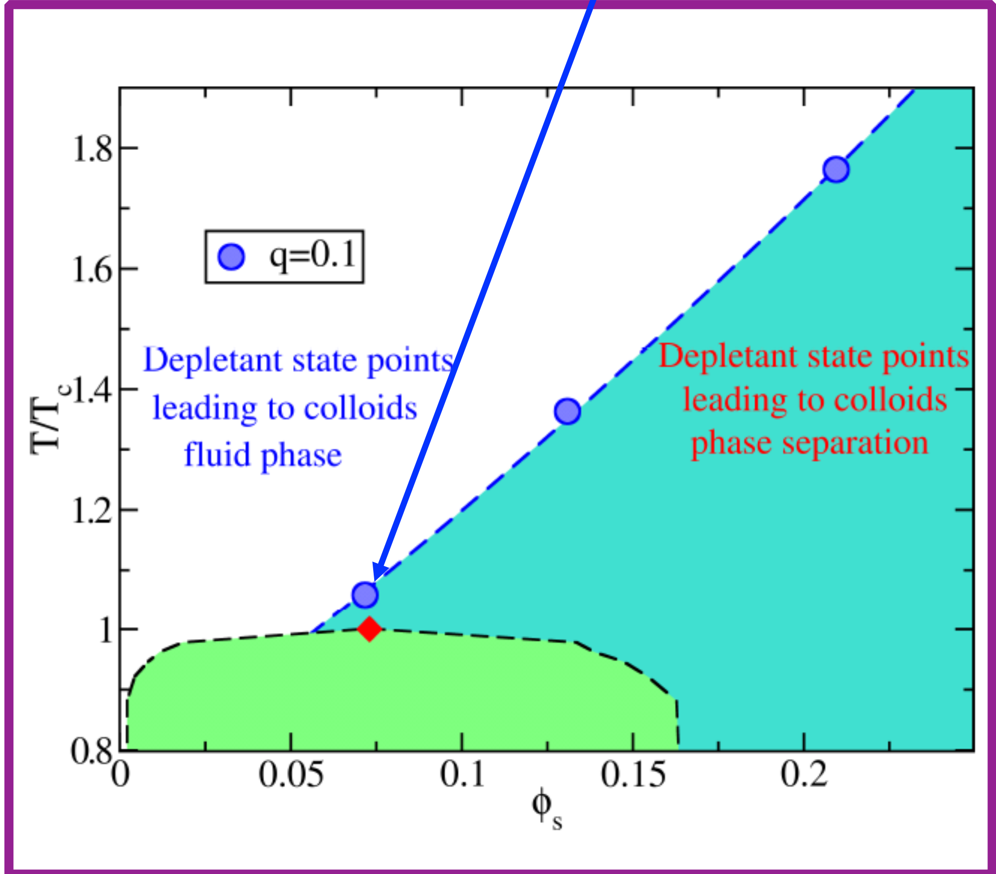
The **correlation length** extracted from the **effective potential coincides** with that of the **bulk critical depletant**

N. Gnan, EZ, P. Tartaglia and F. Sciortino *Soft Matter 8, 1991 (2012)*

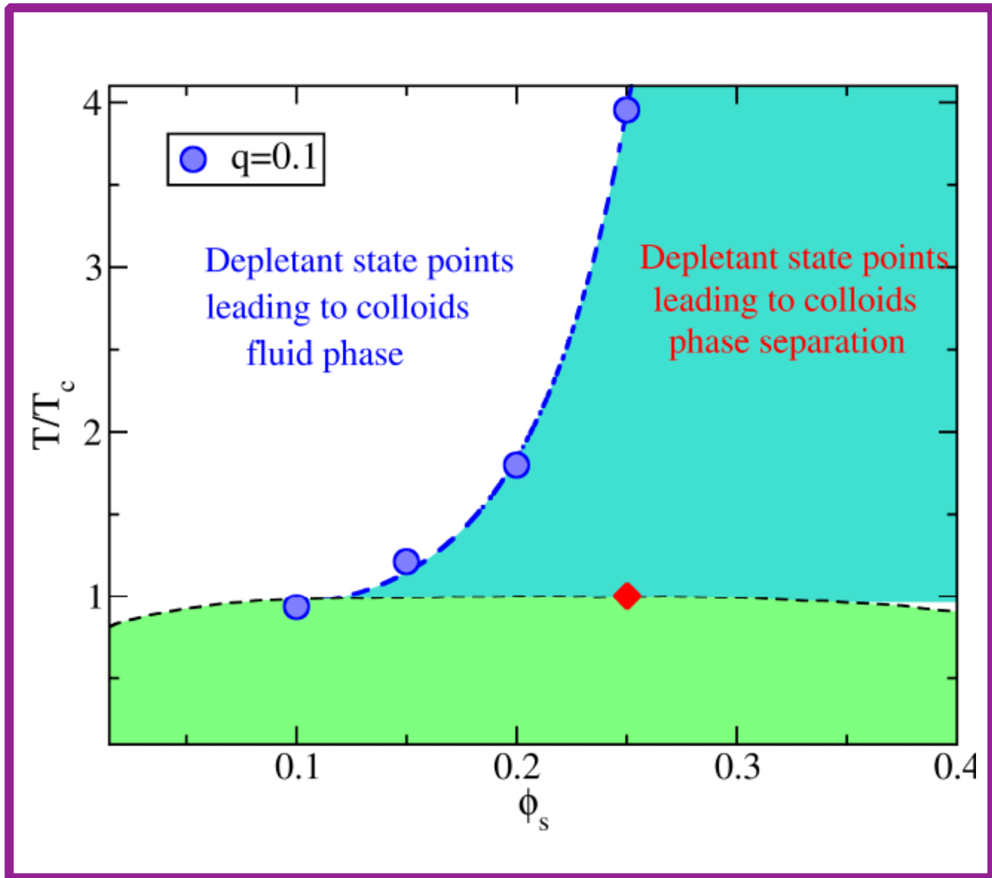
Phase behaviour of colloids: role of the depletant



Critical Casimir forces contribute to colloidal aggregation



patchy depletant



SW depletant

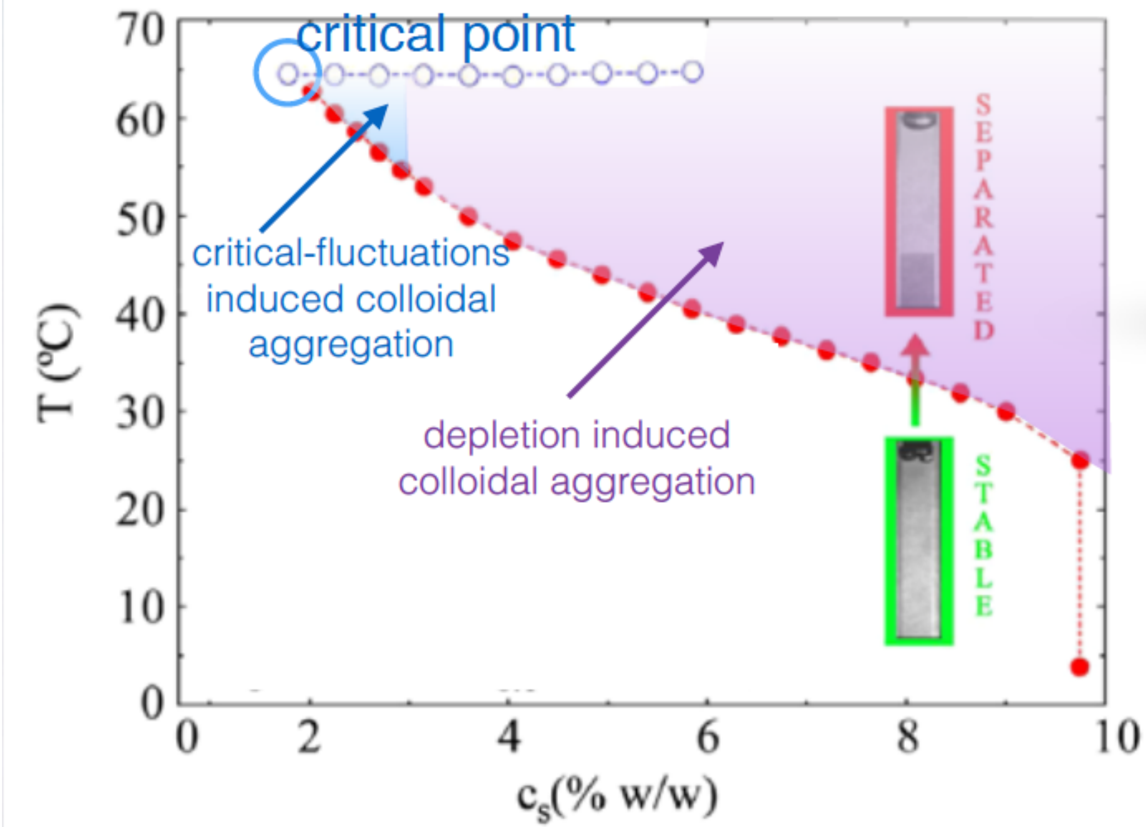
Critical depletion?

PRL **105**, 198301 (2010) PHYSICAL REVIEW LETTERS week ending 5 NOVEMBER 2010

Critical Depletion

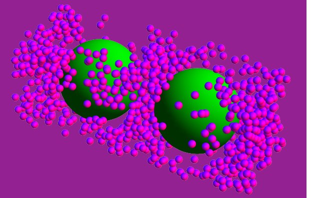
Stefano Buzzaccaro,[1] Jader Colombo,[2] Alberto Parola,[2] and Roberto Piazza[1]

"…we have shown that **depletion** interactions **and fluctuation induced forces near a critical point** have a **common physical origin**…"



Still controversial, but…

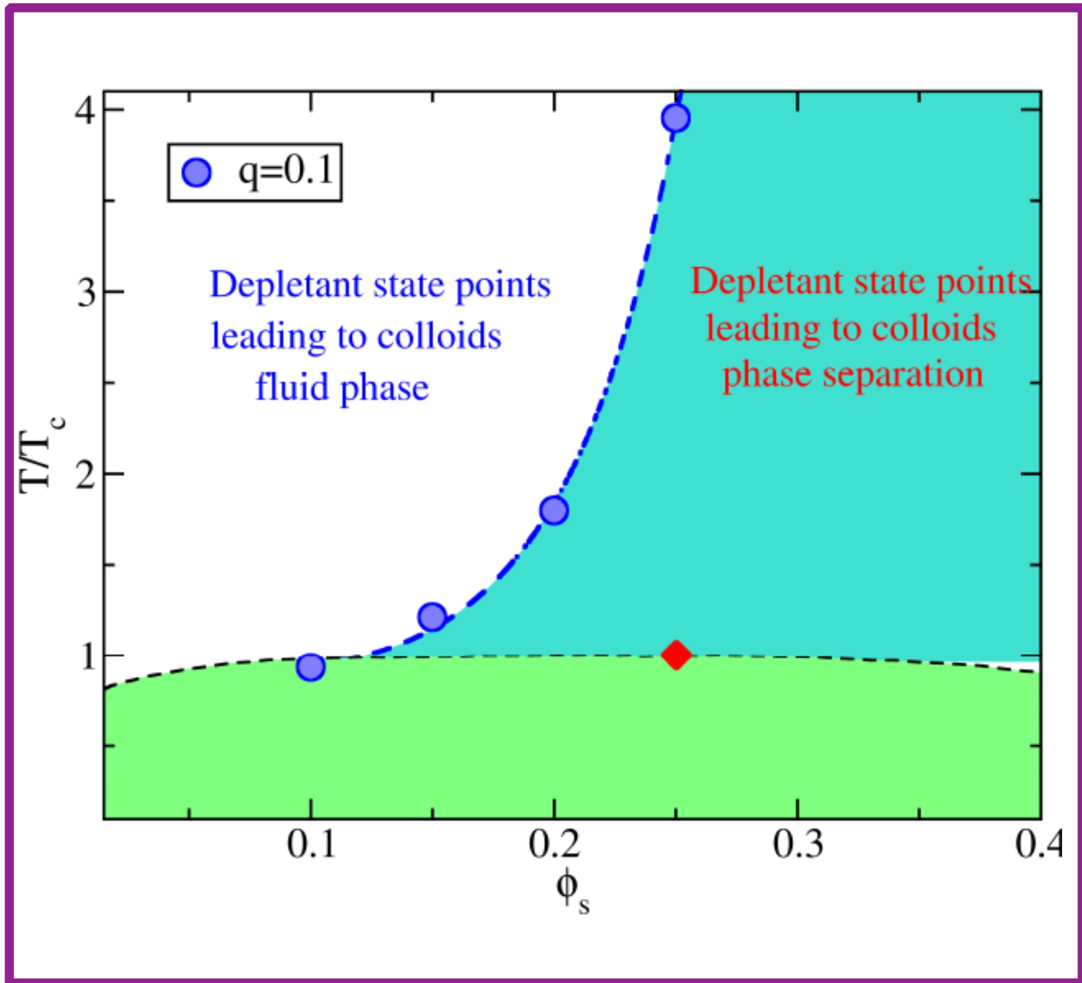
Phase separation of colloids: role of the depletant



- Grand-canonical MC simulations of a **single component system of colloidal particles** interacting via the Hamiltonian

$$H = \sum_{ij} V_{HS}(r_{ij}) + V_{\mathrm{eff}}(r_{ij})$$

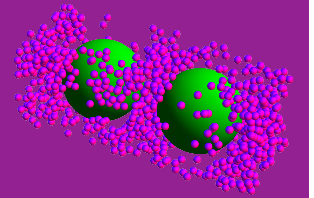
- We **scan the chemical potential** in order to detect if colloids form a **stable fluid phase or phase separate**



q= size ratio

SW depletant

Phase separation of colloids: role of the depletant



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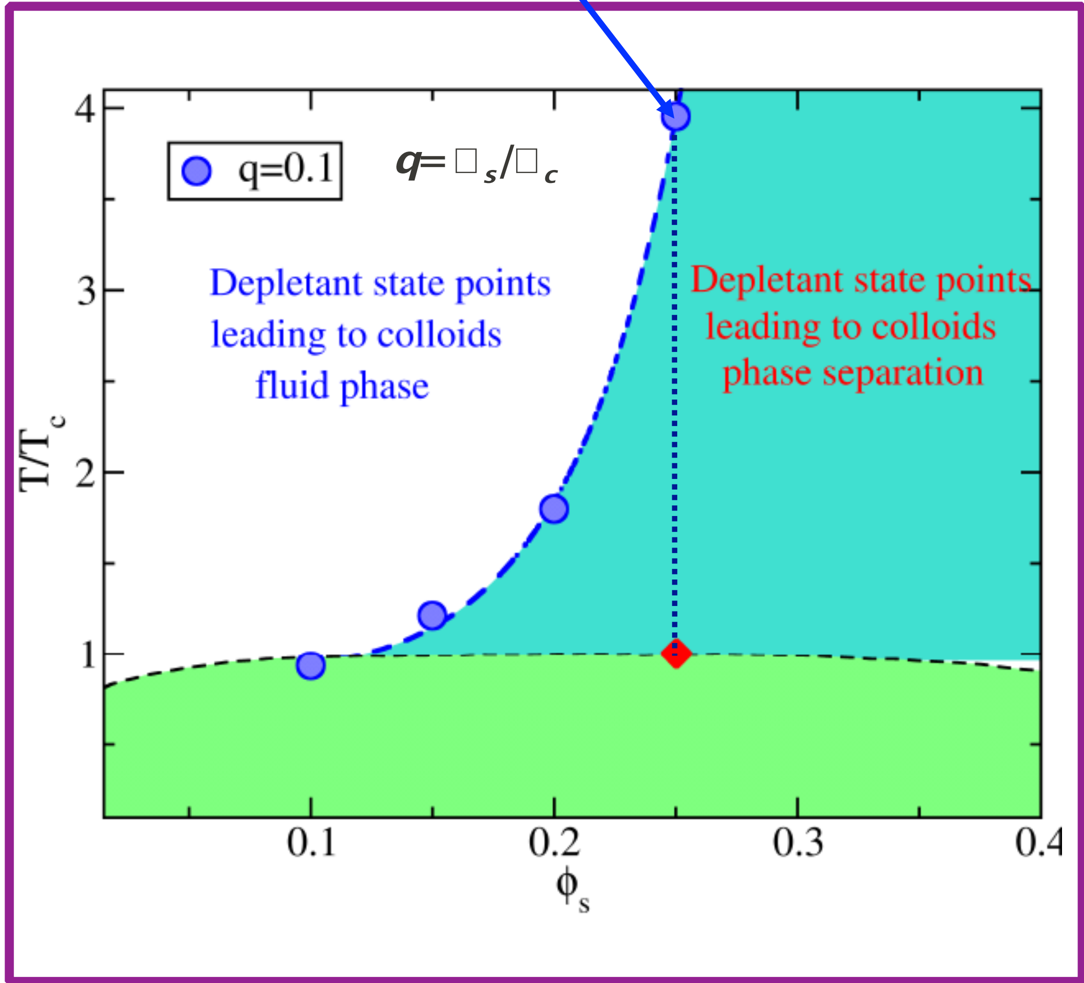
Colloidal aggregation takes place before critical forces arise!

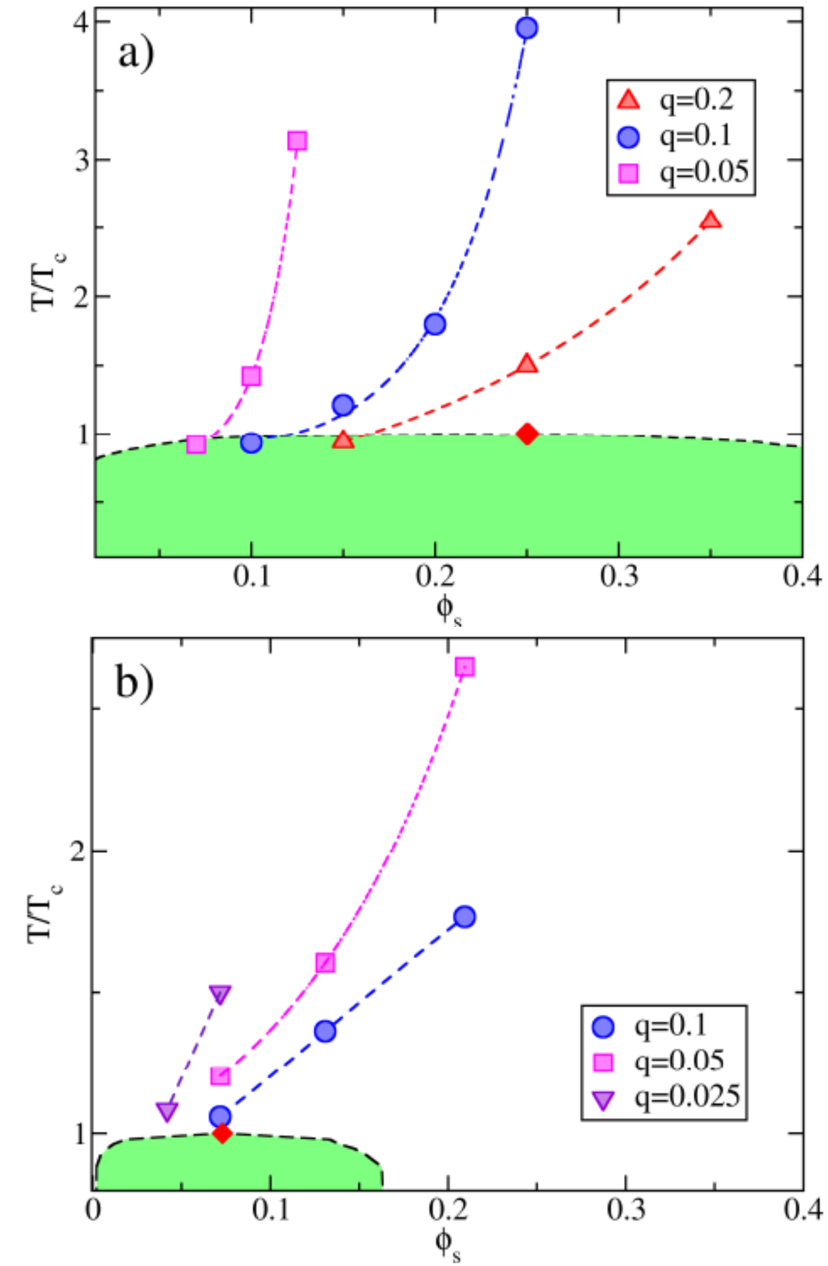


SW depletant

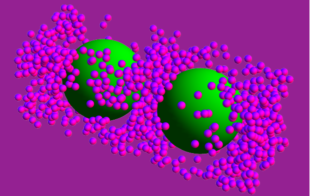
Phase separation of colloids: role of the depletant size

- We evaluate the loci of the onset of phase separation for different *q* values

- Our results suggest that f**or small *size ratios*** it is difficult to observe Casimir-induced colloidal phase separation (**depletion** drives phase separation!)



Phase separation of colloids: role of the depletant size



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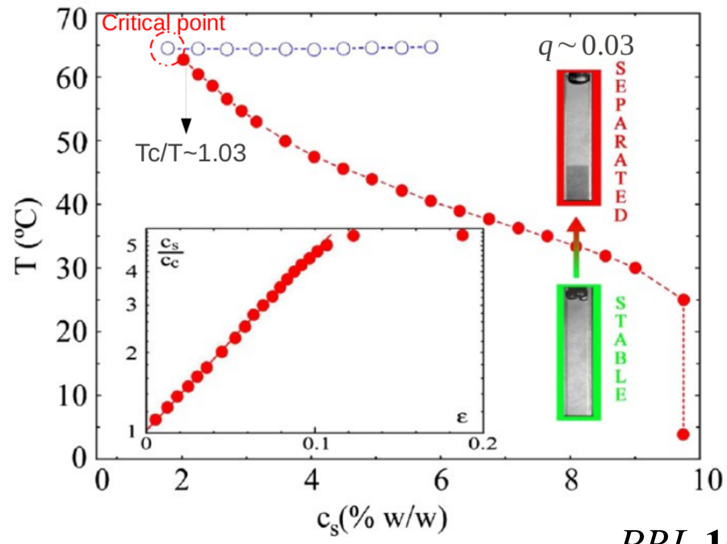
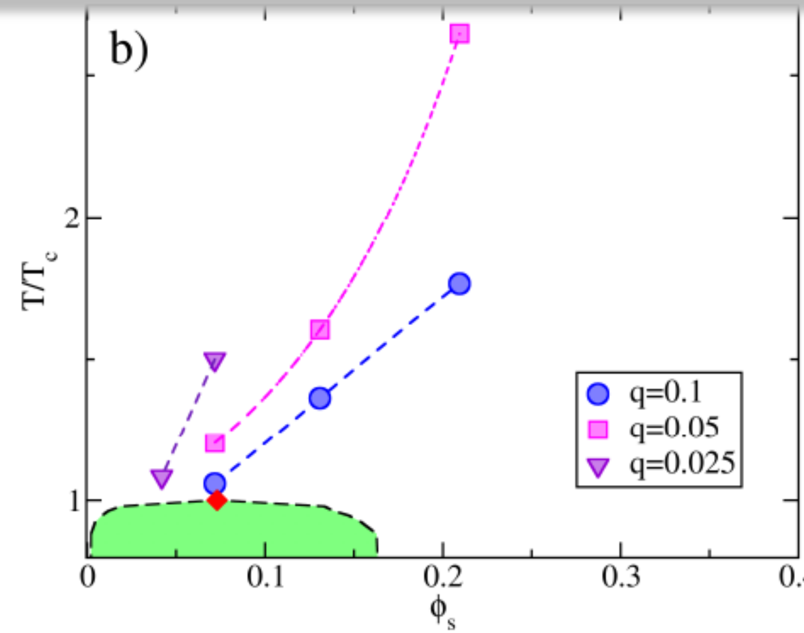
How can the experiment reveal Casimir-induced phase separation with $q_{exp} \sim 0.03$?

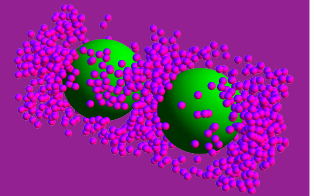


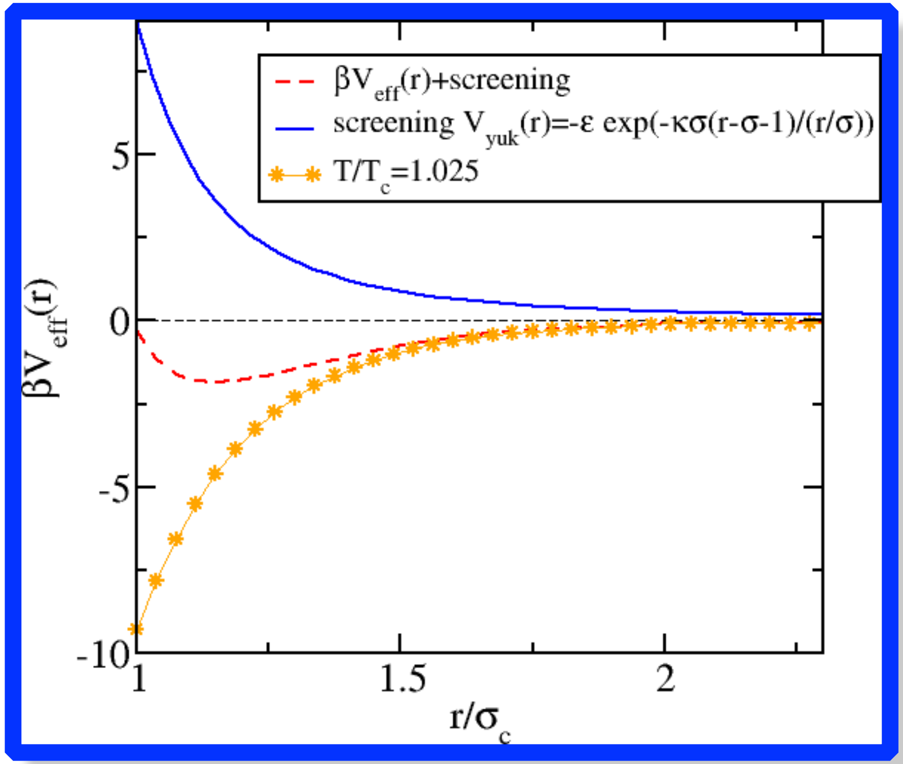
particles with a radius R ~ 90 nm made of MFA in a solvent of non ionic micelles of radius r~3 nm

PRL **105**, (2010)

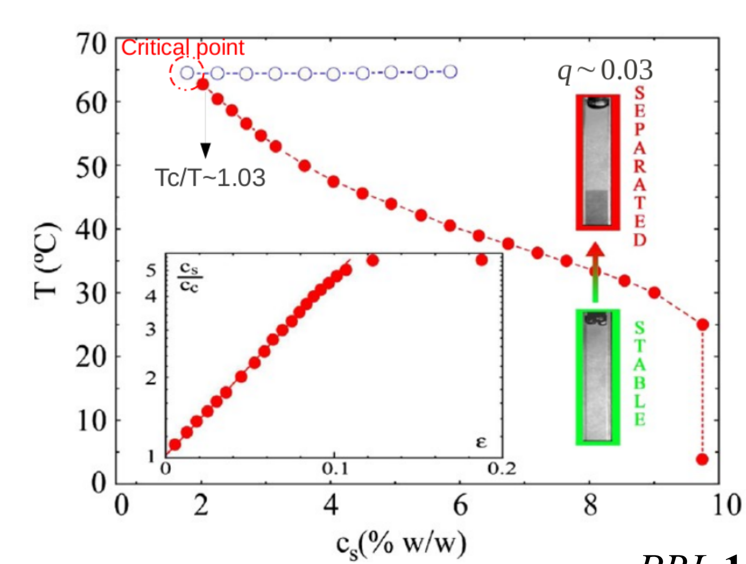


Phase separation of colloids: role of the depletant size



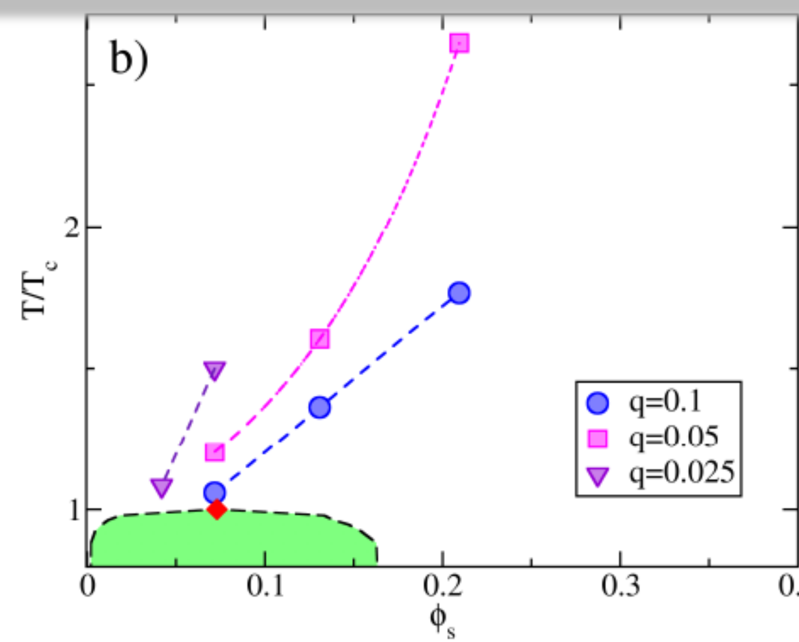


when additional repulsive interaction compensates the depletion part the onset of aggregation occurs close to the critical point

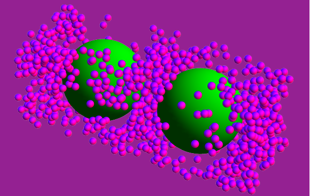


particles with a radius R ~ 90 nm made of MFA in a solvent of non ionic micelles of radius r~3 nm

PRL **105**, (2010)



Effects of depletant-colloid interactions



- The Hamiltonian of the system simulated is

$$H = V_{CC} + V_{SS} + V_{CS}$$

So far

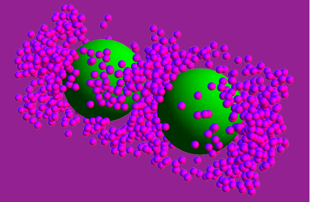
- V_{cc} = **HS** potential
- V_{ss} = **SW** or **3P** potential
- **V_{cs} =HS potential**

Symmetric BC

- V_{cc} = **HS** potential
- V_{ss} = **SW**
- V_{c1s} =**HS** potential
- V_{c2s} =**SW** potential

Antisymmetric BC

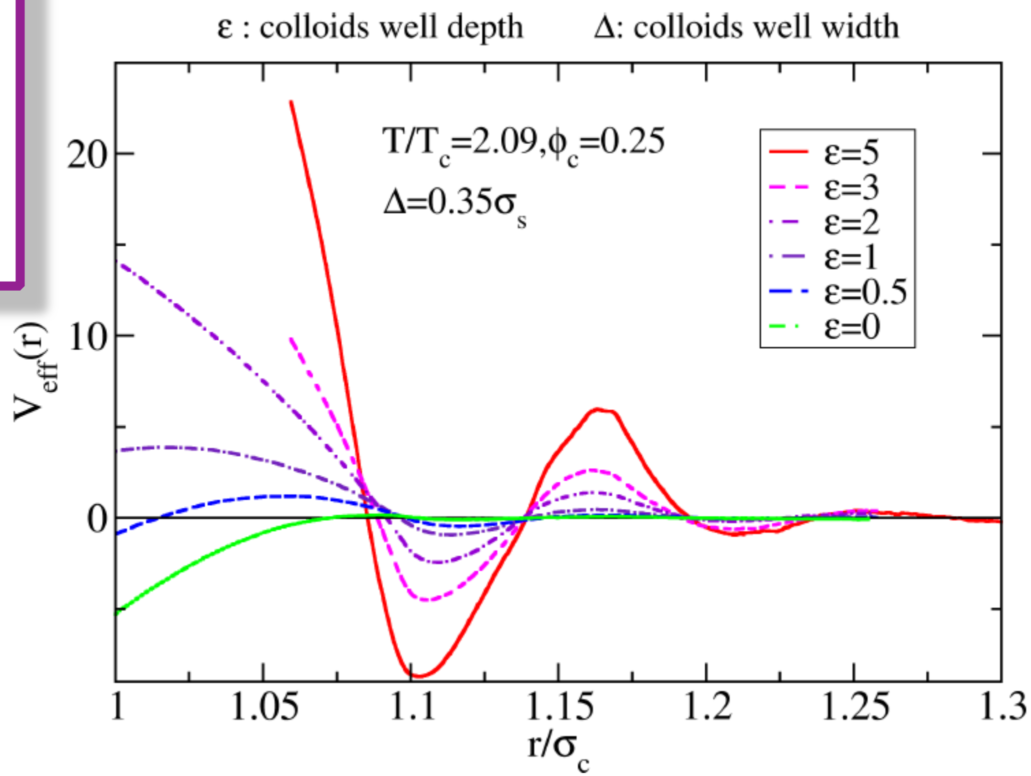
Depletant-colloid interactions: effective potentials for symmetric BC



- V_{cc} = **HS** potential
- V_{ss} = **SW** potential, ($\Delta=0.1\sigma_s$, $\varepsilon_s=1$)
- V_{cs} =**SW** potential

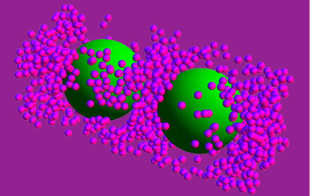
- Increasing the strength of the interaction, the short range part of the potential becomes repulsive and large oscillations appears

High Temperature



N. Gnan, EZ and F. Sciortino *J. Chem. Phys. 137, 084903 (2012)*

Depletant-colloid interactions: effective potentials for symmetric BC



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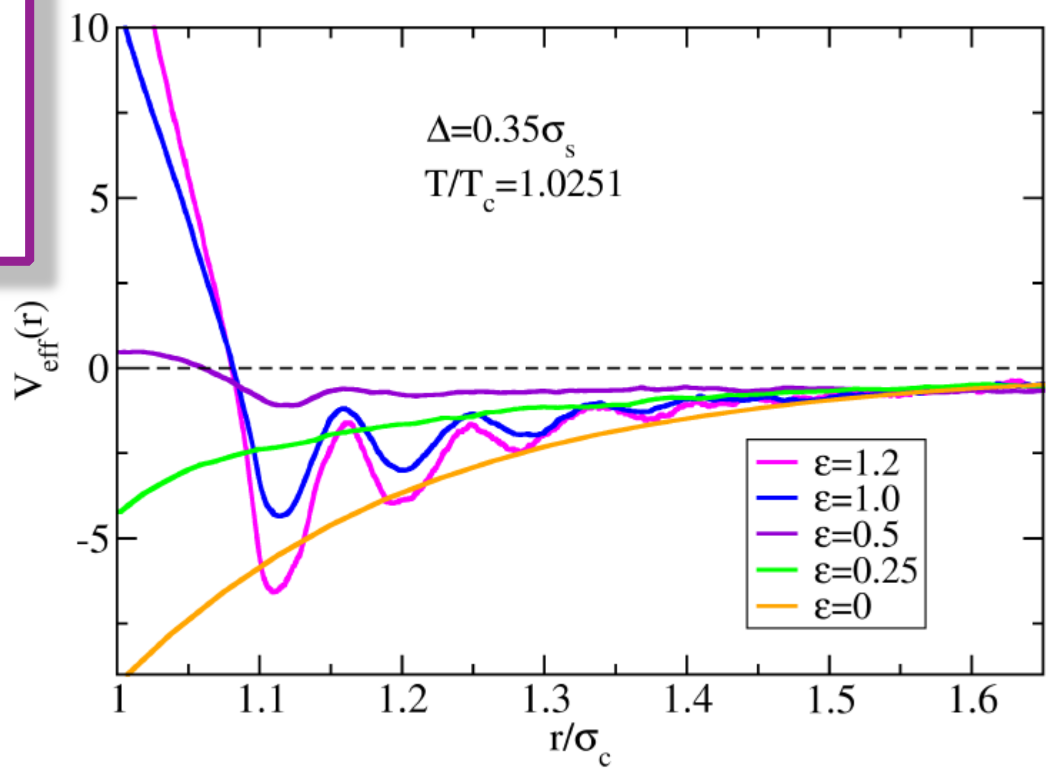
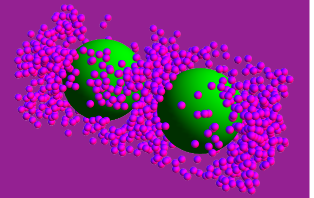
Low Temperature



- Increasing the strength of the interaction, the short range part of the potential becomes repulsive and large oscillations arise
- Close to the critical point a long range exponential part appears in the potential

N. Gnan, EZ and F. Sciortino *J. Chem. Phys. 137, 084903 (2012)*

Depletant-colloid interactions: effective potentials for antisymmetric BC

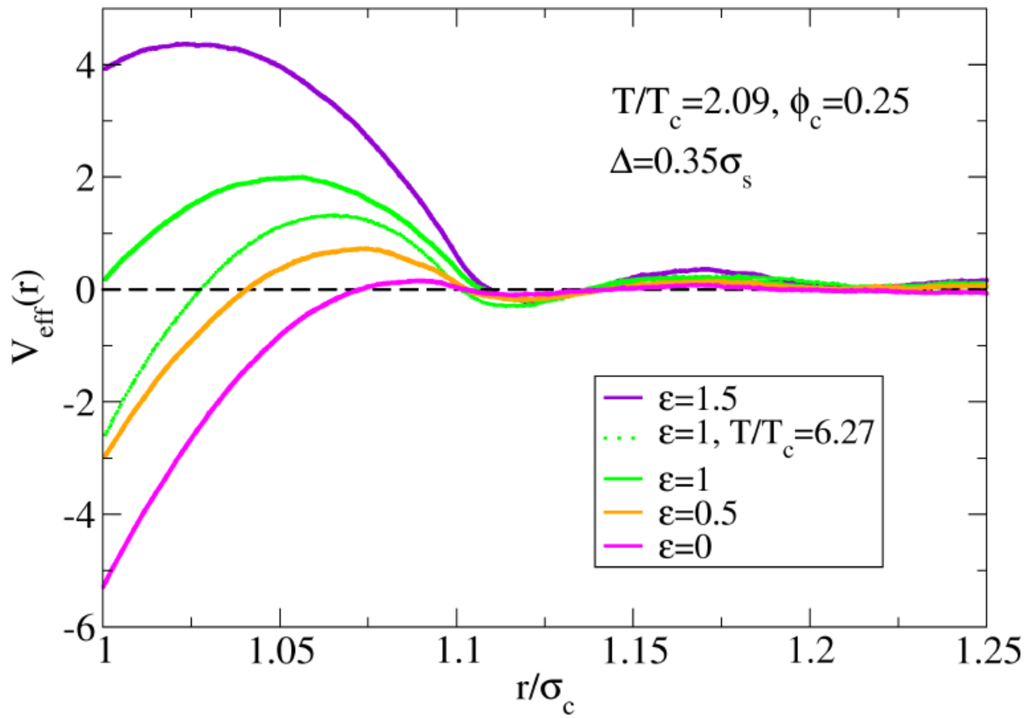


- V_{cc} = **HS** potential
- V_{ss} = **SW**
- V_{c1s} =**HS** potential
- V_{c2s} =**SW** potential

Antisymmetric BC

- Increasing the strength of the interaction, the short range part of the potential becomes repulsive
- No large oscillation appear

High Temperature



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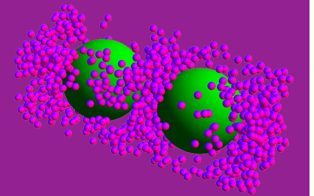
Depletant-colloid interactions: effective potentials for antisymmetric BC



- V_{cc} = **HS** potential
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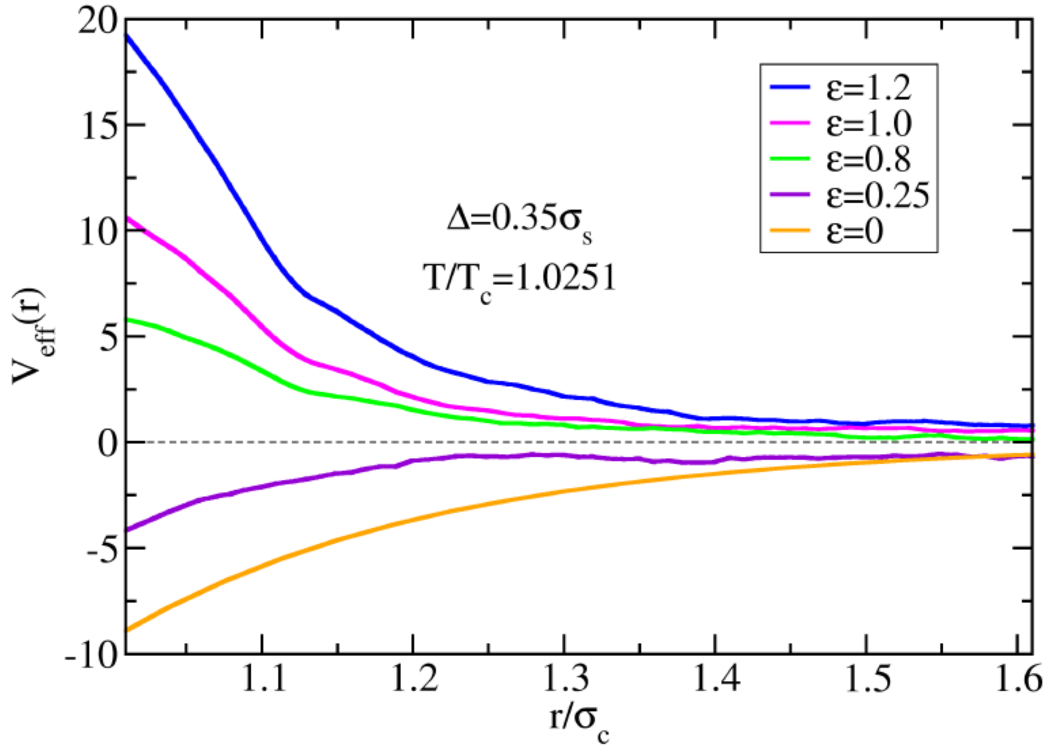
Antisymmetric BC

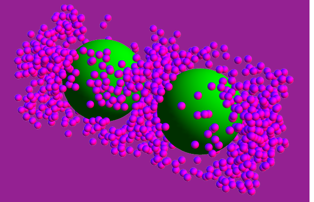
Low Temperature



- Increasing the strength of the interaction, the **whole potential becomes repulsive**
- The **characteristic length** is still **consistent with** the thermal correlation length ξ

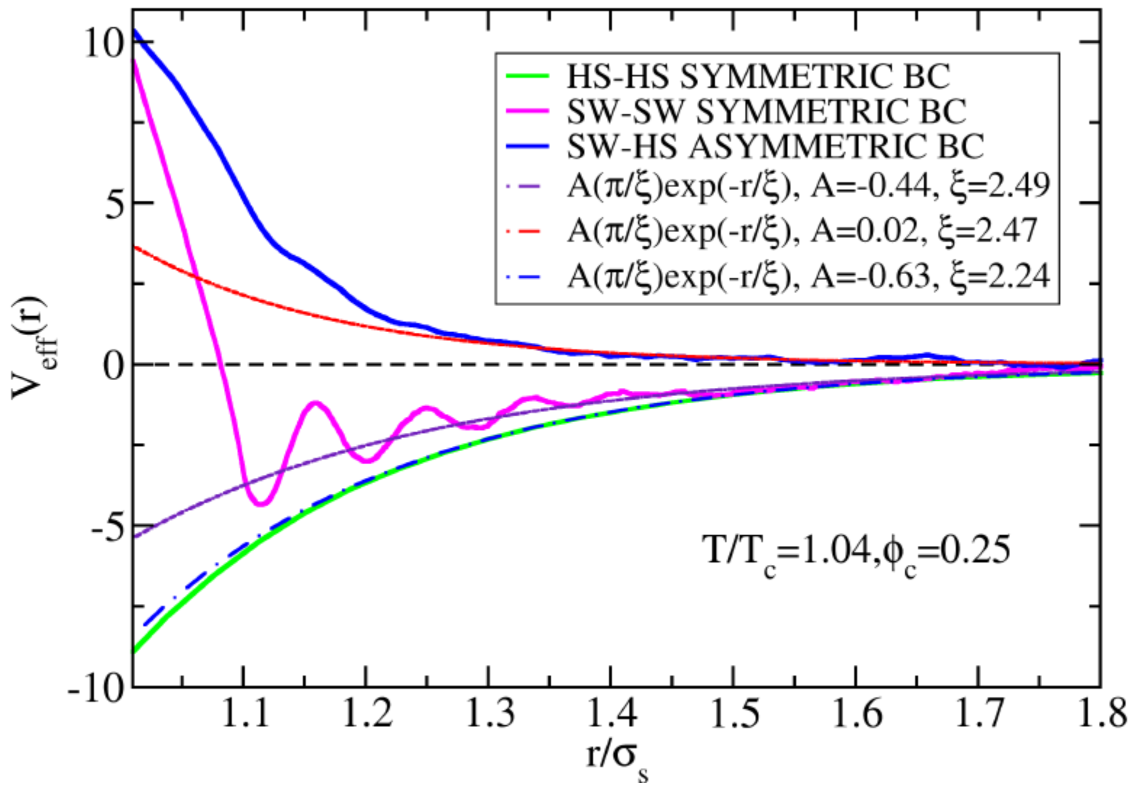
N. Gnan, EZ and F. Sciortino *J. Chem. Phys. 137, 084903 (2012)*

Depletant-colloid interactions: effective potentials and boundary conditions



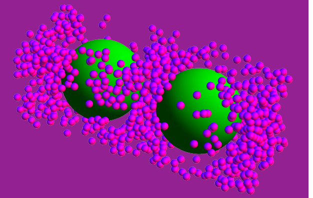
- In the critical region, **indipendently on the BC**, the long range part of the effective potential decays **exponentially**.

- The **characteristic length** of the potential is **consistent with** the correlation length ξ



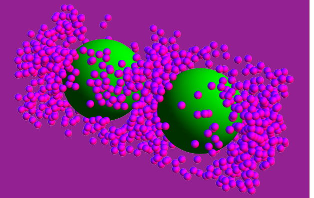
N. Gnan, EZ and F. Sciortino *J. Chem. Phys. 137, 084903 (2012)*

A step forward ...



Can we induce long-range effective forces with another mechanism?

A step forward ...



Can we induce long-range effective forces with another mechanism?

GEOMETRIC PERCOLATION

- Describes the **growth of clusters** on approaching the percolation threshold. **At p_c** an **infinite cluster** appears

THERMAL CRITICAL PHENOMENA

- Describes the **growth of correlated regions** on approaching a 2nd order critical point. **At T_c** the size of the correlated regions **diverge**.

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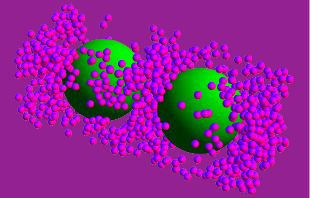

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THERMAL CRITICAL PHENOMENA

- Describes the **growth of correlated regions** on approaching a 2nd order critical point. **At T_c** the size of the correlated regions **diverge**.

- **Both are characterized by scaling and universality**

The **connectivity length** diverges at the transition

$$\xi_{conn} \propto |p - p_c|^{-\nu_{RP}}$$

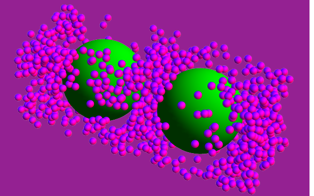
RP: random percolation universality class

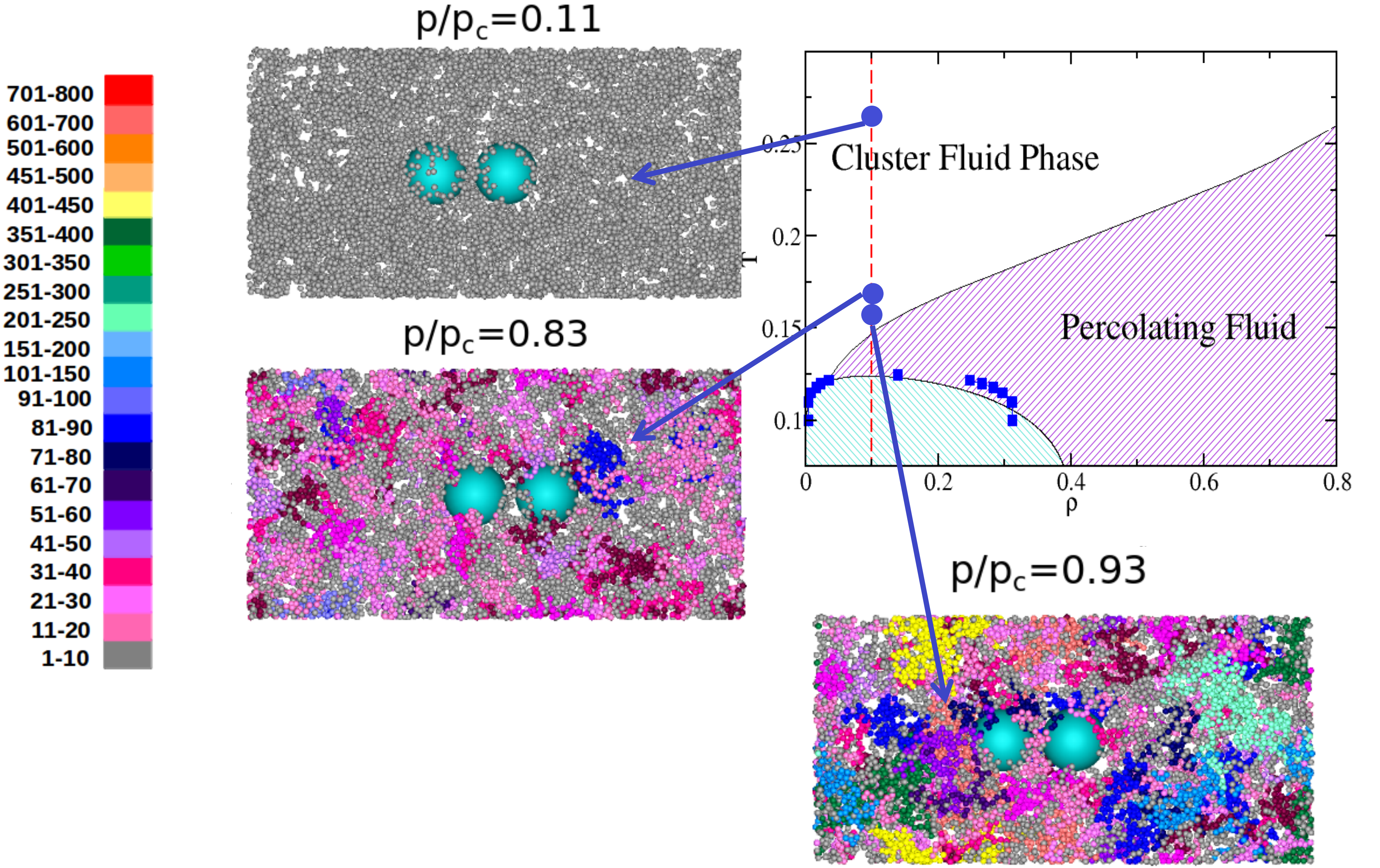
The **correlation length** diverges at the critical point

$$\xi_{corr} \propto |T - T_c|^{-\nu_{IS}}$$

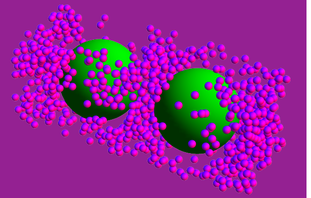
IS: Ising universality class

Effective interactions between 2 HS colloids immersed in a fluid of clusters





Depletant model for simulations: two important facts

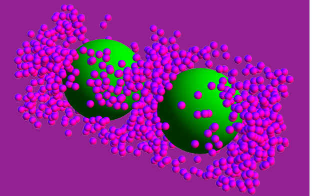


1) Percolation can be mapped into a critical point only if the system is characterized by quenched disorder [*M. Daoud , A. Coniglio, J. Phys. A: Math. Gen. 14, L301 (1981).*]

Quenched disorder ⟺ **Irreversible bonds**
(chemical gel)

The bond lifetime does not need to be infinite, but larger than the observation time

Depletant model for simulations: two important points



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Quenched disorder ⟺ **Irreversible bonds**
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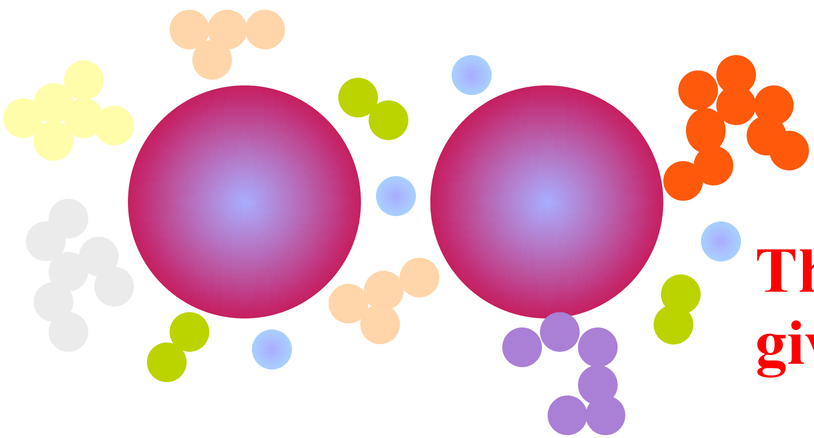
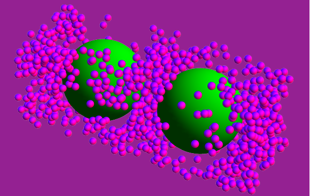
2) What plays the role of critical fluctuations in percolation?



the two colloids interact with clusters whose size fluctuates

The confinement of such fluctuations should give rise to a long-range effective interaction
Casimir-like effect

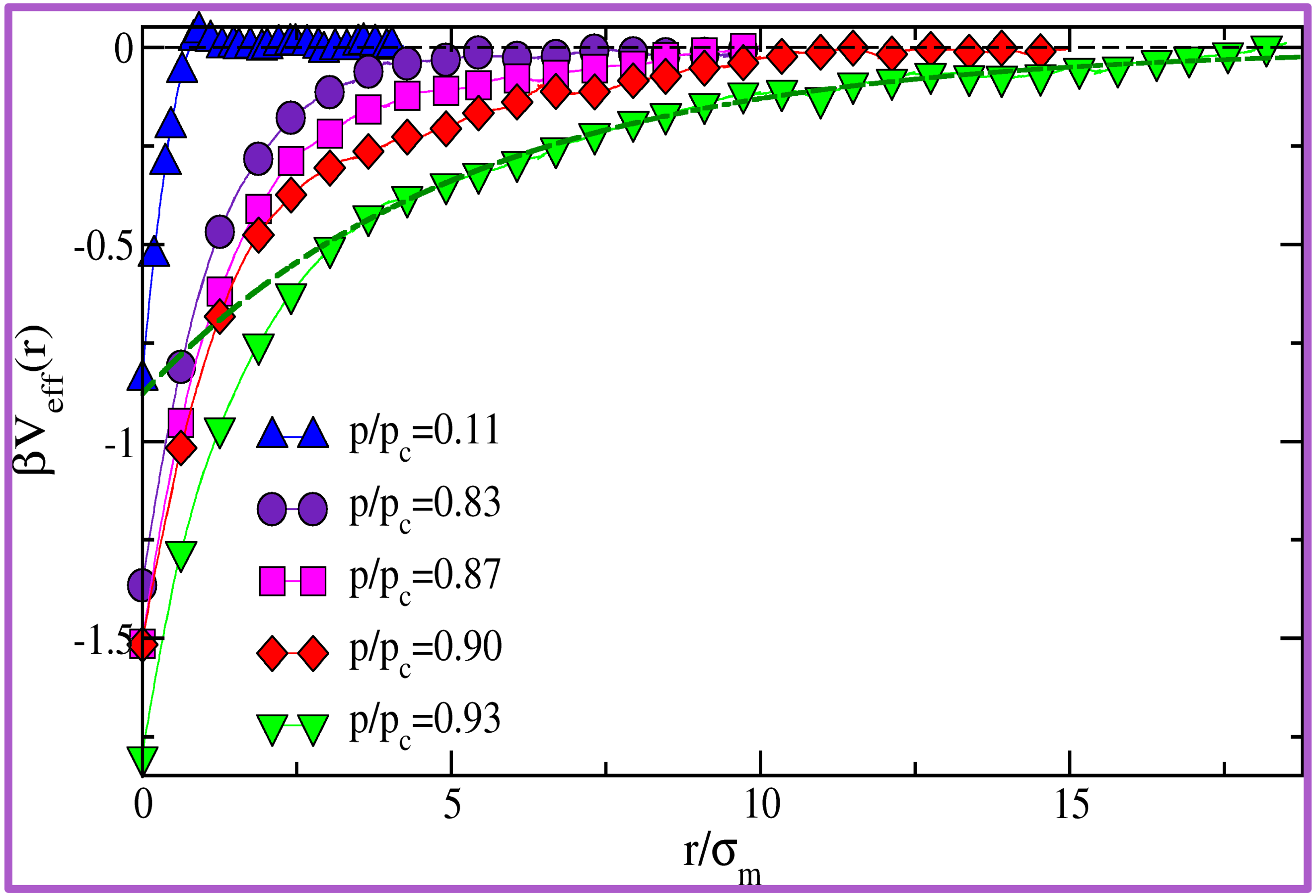
Results: Effective Potentials close to percolation



- V_{eff} turns into a **completely attractive** potential

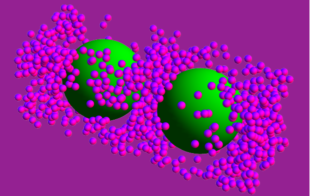
- A progressive significant **increase of the interaction range** is observed on approaching the percolation threshold

Φ=0.052



N. Gnan, EZ and F. Sciortino, Nat. Comm. 5, 3267 (2014)

Results: Effective Potentials close to percolation



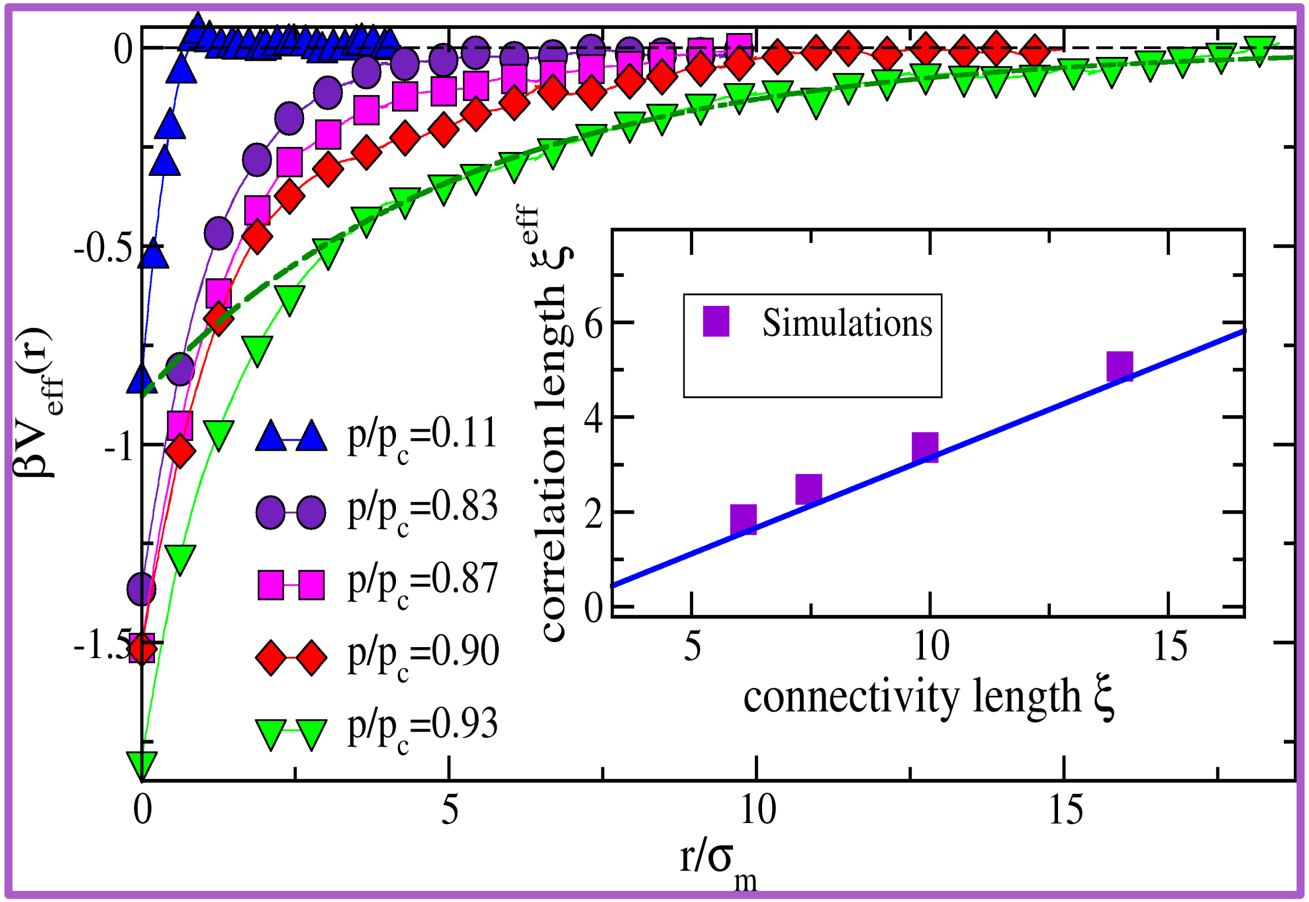
The long-distance part of V*eff* is well described by an exponential function

exp(-r/ξeff)

controlled by a length that is proportional to **the connectivity length** of the sol of clusters

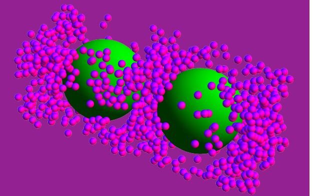
$$\xi = \left[\frac{2\sum_s R_g^2(s)s^2n(s)}{\sum_s s^2n(s)}\right]^{1/2}$$

Φ=0.052

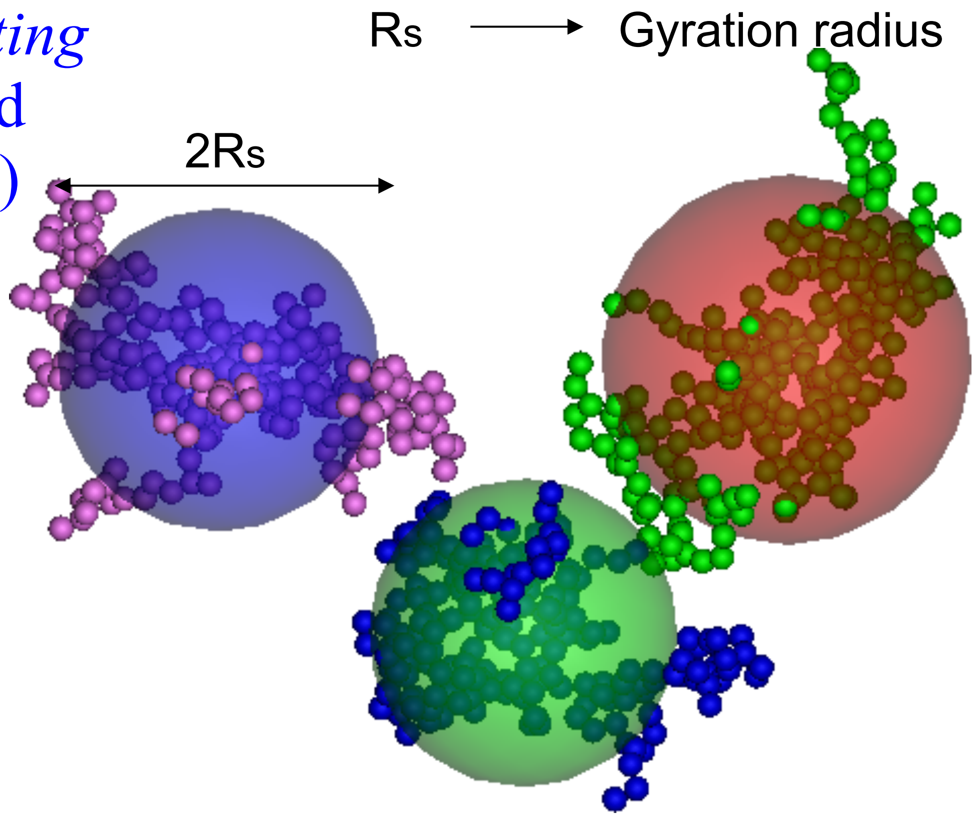


N. Gnan, EZ and F. Sciortino, Nat. Comm. 5, 3267 (2014)

Theory: a polydisperse Asakura-Oosawa model



We model the sol of clusters as *non-interacting* polydisperse spheres of radius Rs distributed according to the cluster size distribution n(s)



$$n(s) = \frac{N s^{-\tau} e^{-\frac{s}{s_c}}}{s_c^{2-\tau}\Gamma(2-\tau, s_c^{-1})}$$

Summing the AO contribution over all clusters:

$$\beta V_{AO}^{eff}(r) = \sum_s \beta V_{AO}(r, R_s, \rho_s) n(s)$$

$$\beta V_{AO}^{eff}(r) = -\pi \int_{(\frac{r}{2R_1})^D}^{\infty} ds \rho_1 \frac{s^{-\tau} e^{-\frac{s}{s_c}}}{s_c^{2-\tau}\Gamma(2-\tau, s_c^{-1})}$$

$$(2R_s - r)\left[\left(\frac{R_s\sigma_c}{2} + \frac{2R_s^2}{3}\right) - \frac{r}{2}\left(\frac{\sigma_c}{2} + \frac{R_s}{3}\right) - \frac{r^2}{12}\right]$$

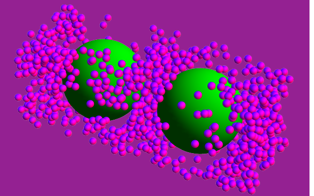
ρ_1 is the monomer number density

and

$R_s = R_1 s^{1/D}$ from percolation theory which holds for s >50

N. Gnan, EZ and F. Sciortino, Nat. Comm. 5, 3267 (2014)

Comparison between theory and simulations

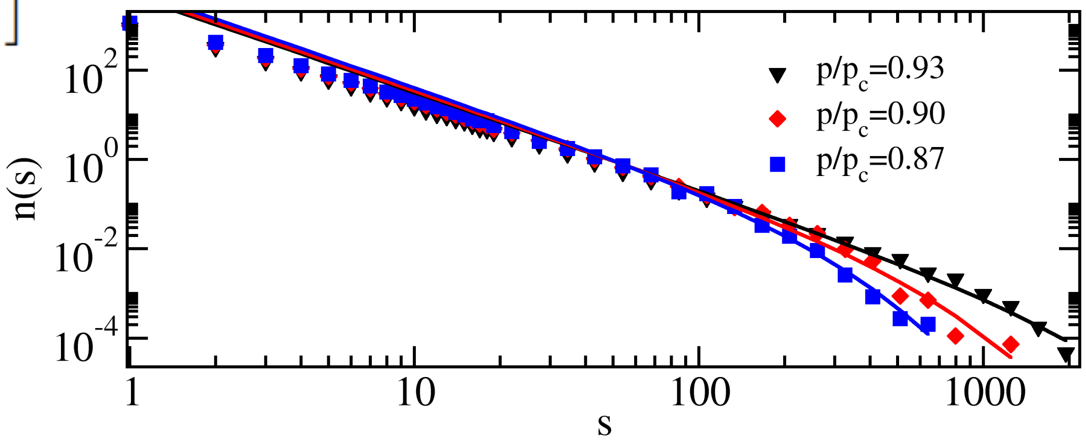


Highly polydisperse AO model

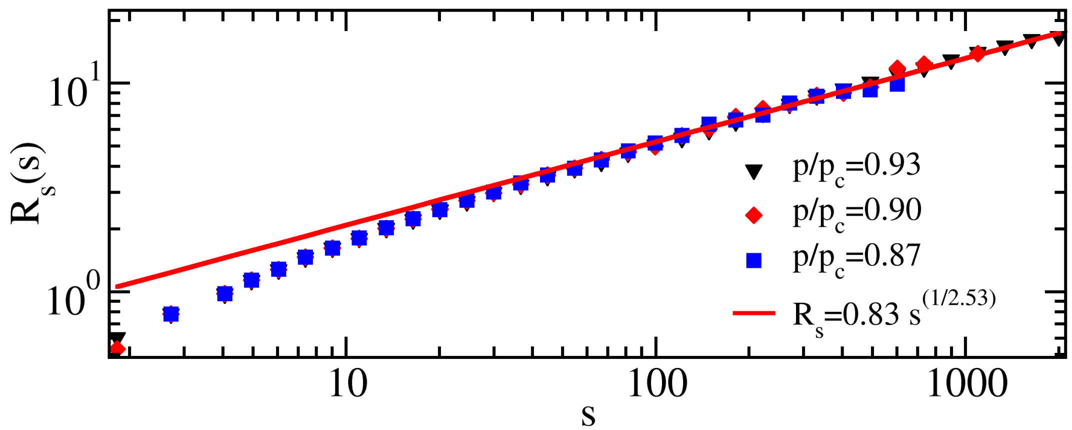
$$\beta V_{AO}^{eff}(r) = -\pi \int_{\left(\frac{r}{2R_1}\right)^D}^{\infty} ds \rho_1 \frac{s^{-\tau} e^{-\frac{s}{s_c}}}{s_c^{2-\tau}\Gamma(2-\tau, s_c^{-1})}$$
$$(2R_s - r)\left[\left(\frac{R_s\sigma_c}{2} + \frac{2R_s^2}{3}\right) - \frac{r}{2}\left(\frac{\sigma_c}{2} + \frac{R_s}{3}\right) - \frac{r^2}{12}\right]$$

To compare theoretical predictions with numerical results we need to extract the non universal values entering in the V_{AO}, i.e. s_c and R_1

Note that a theoretical description based on **universal properties** of cluster fluids close to percolation **applies only for** cluster **sizes above 50**



Simulations can be meaningfully compared with theoretical data for r >2Rs(s=50)



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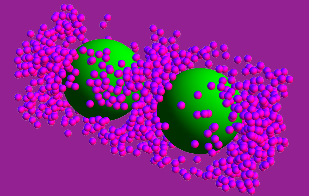
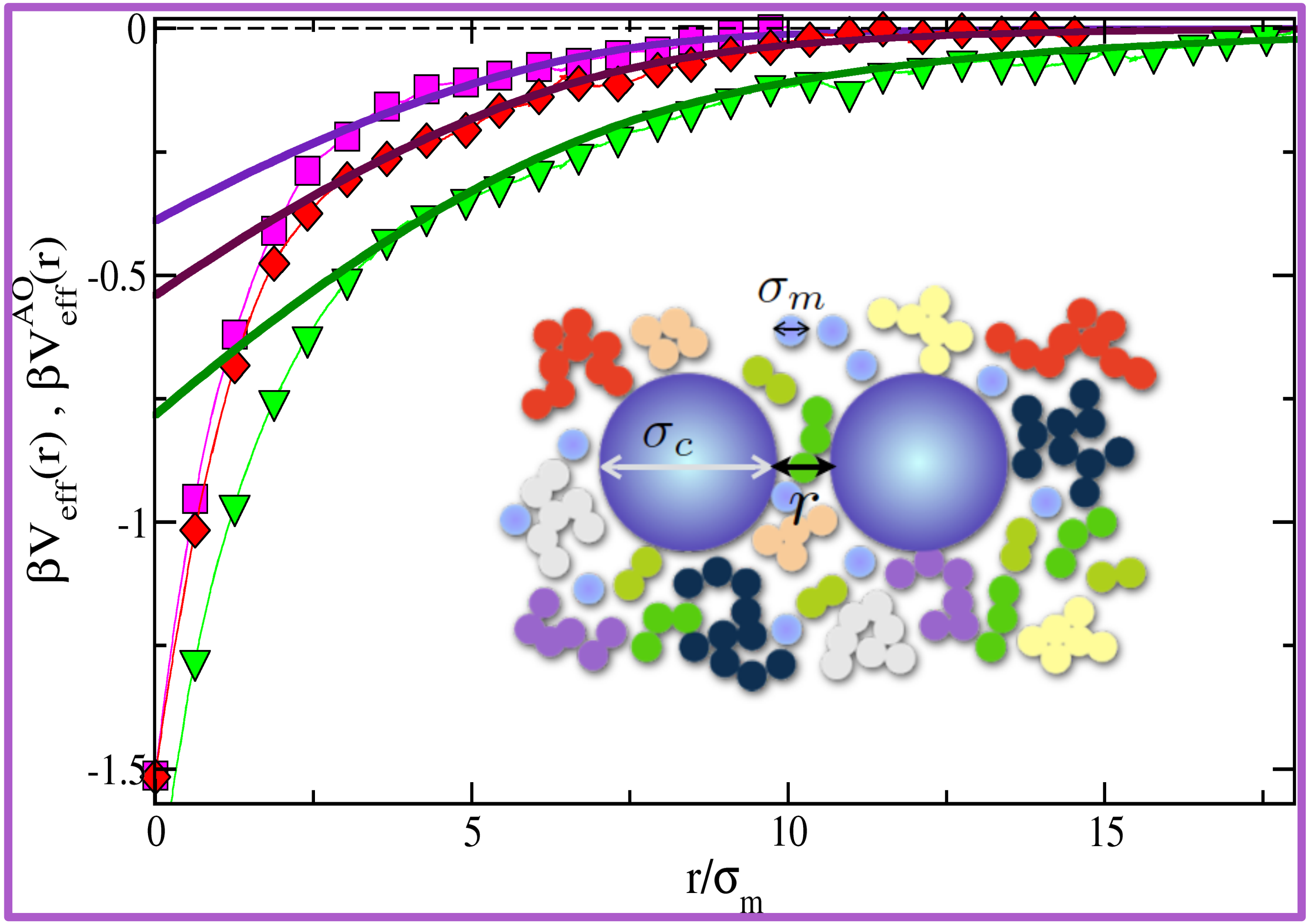


•A surprisingly good agreement is found for r >2Rs(s=50)

• **The effective potential can be assimilated to a depletion interaction** acting on all length scales associated with the clusters



N. Gnan, EZ and F. Sciortino, Nat. Comm. 5, 3267 (2014)

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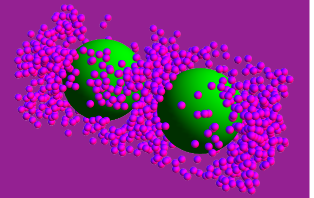
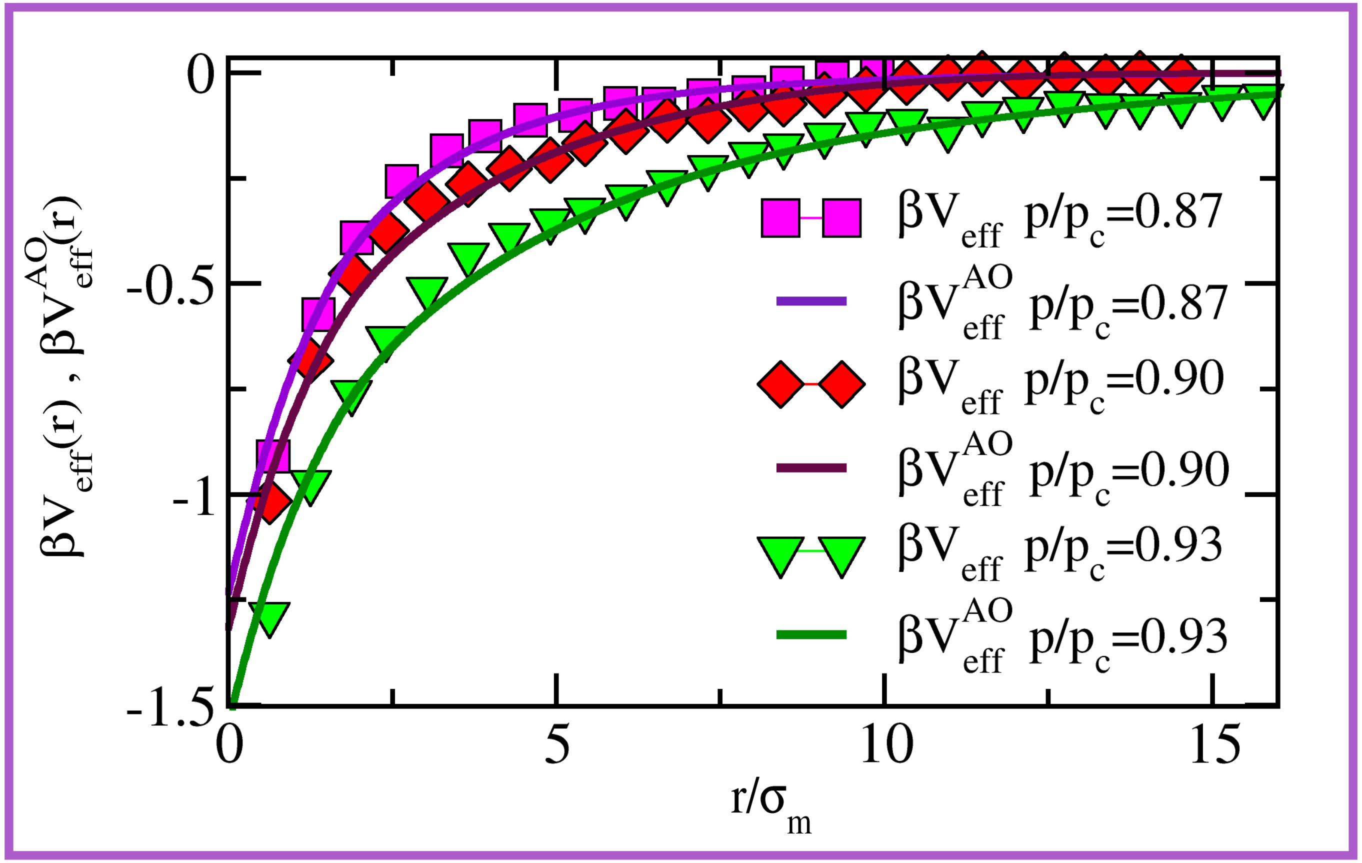
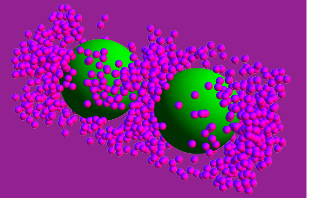


For r <2Rs(s=50)a quantitative agreement can be achieved by using the numerical cluster size configurations in the expression for VAO



N. Gnan, EZ and F. Sciortino, Nat. Comm. 5, 3267 (2014)

Conclusions



- The use of a critical depletant generates ***long-range*** effective forces on colloids and can be exploited to control colloidal aggregation and phase transitions.

- A **long-range effective force** is also found in simulations of two colloids in a depletant **close to the percolation transition**. Such force provides a **geometric** analogue of the critical **Casimir effect.**

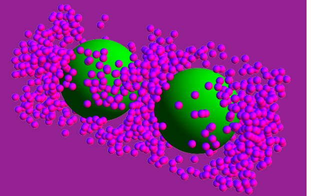
- **The use of** a simple theoretical description based on **a polydisperse AO model** in which clusters are treated as non-interacting spheres **shows** that the mechanism controlling the effective interactions can be assimilated to **a depletion effect.**

Perspectives

- **Role of the lifetime of the clusters. Link with depletion?**

- **Experimental tests?**

Conclusions



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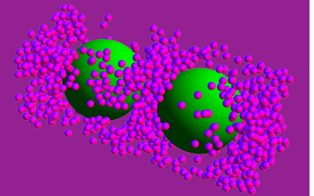
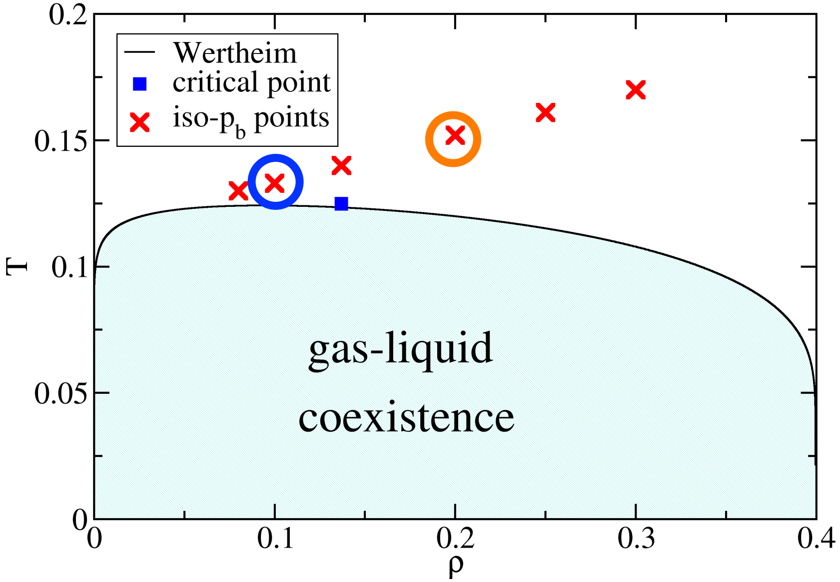
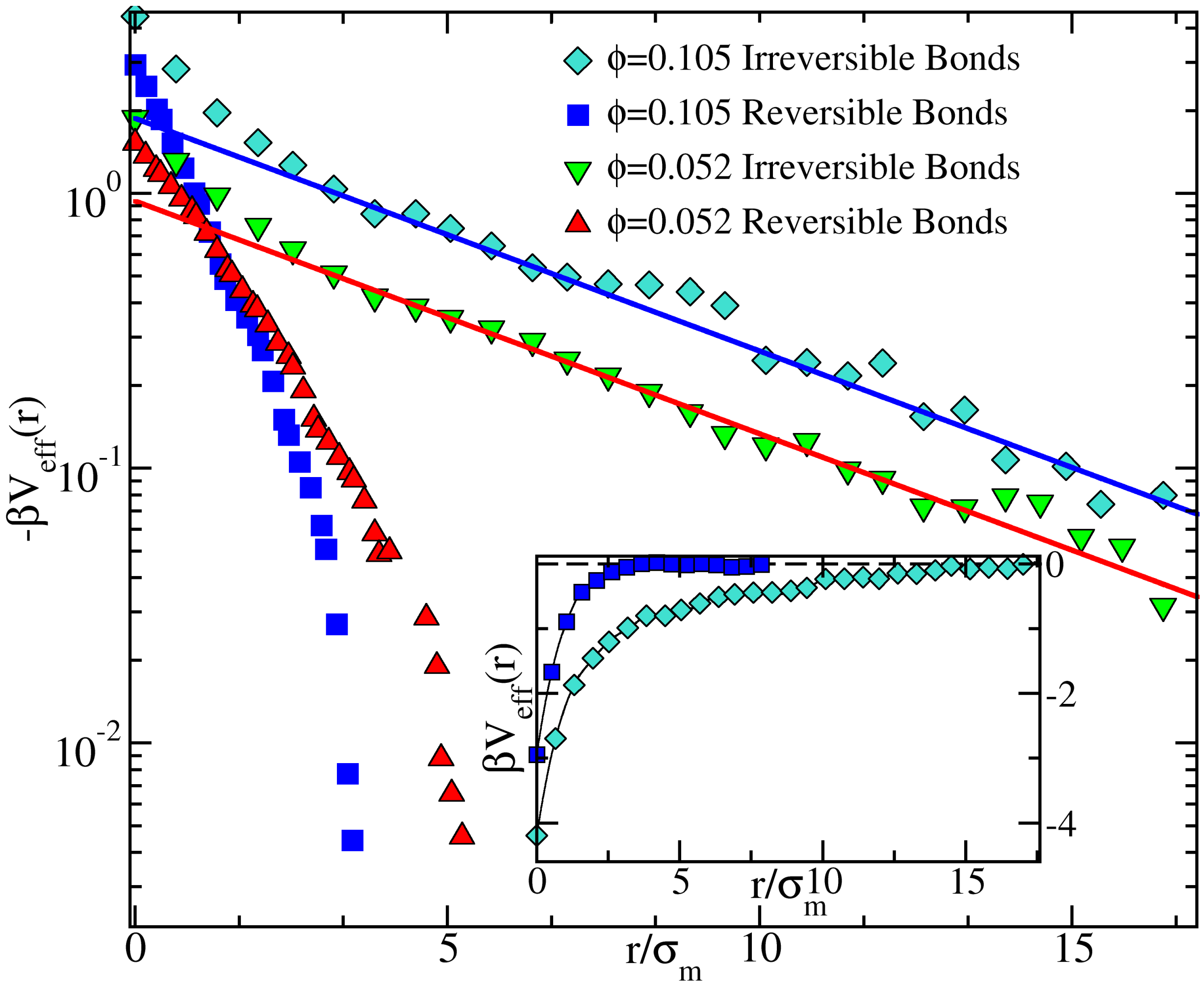
Thank you!

Reversible vs irreversible bonds



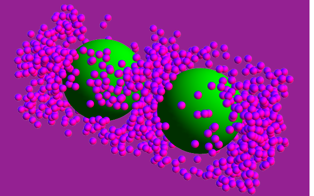


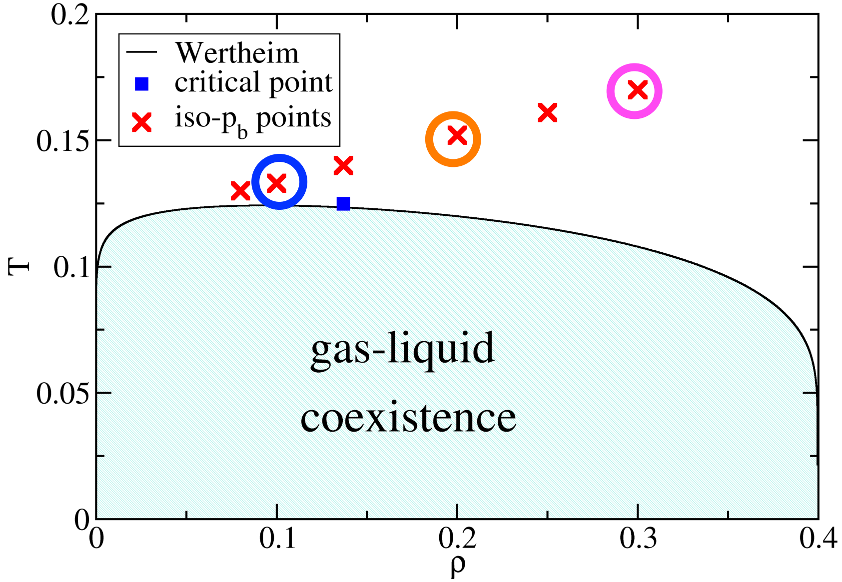
Reversible clusters give rise to an effective force with a much smaller range.

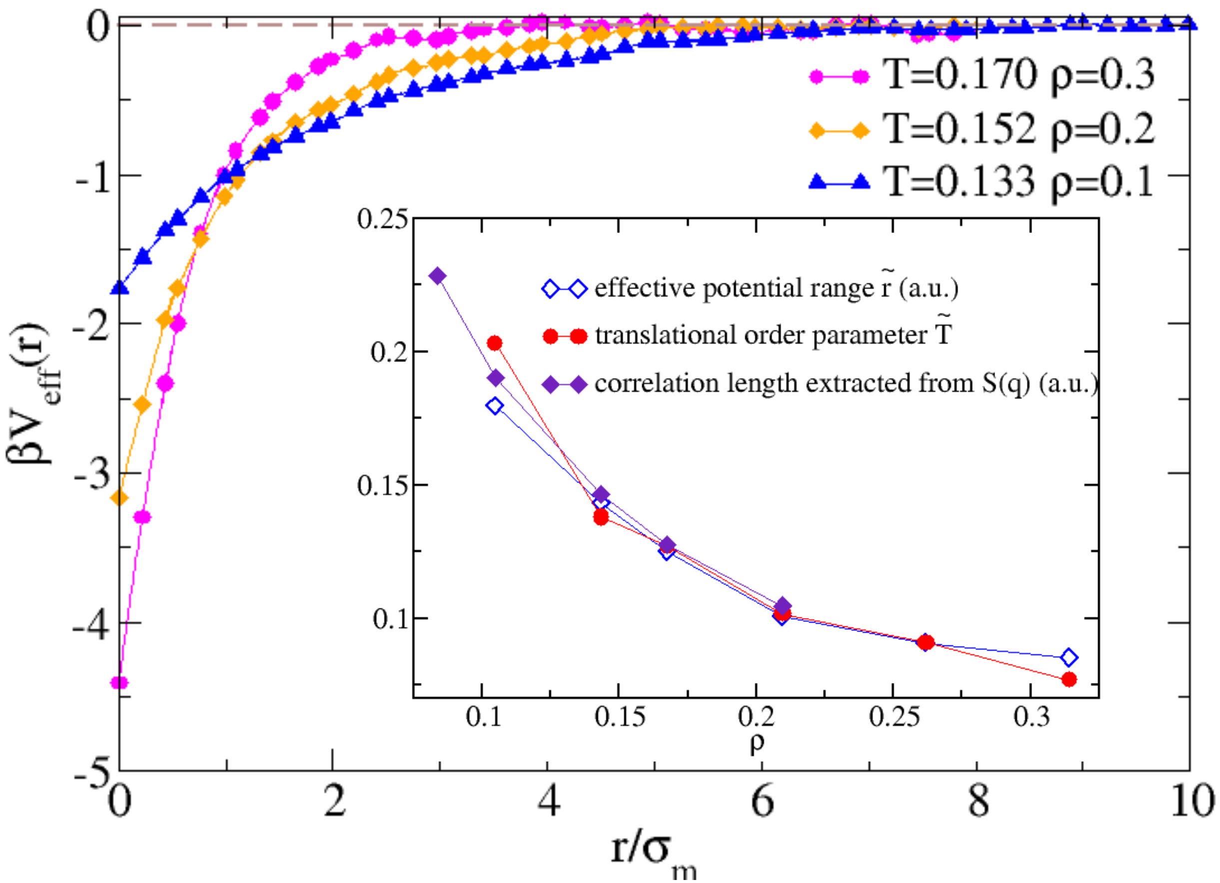


N. Gnan et al in preparation

Reversible vs irreversible bonds







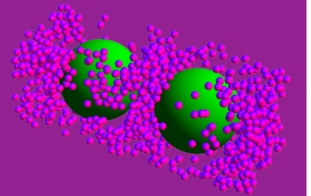
The range of the potential is controlled by the thermal correlation length, which can be measured by the translational order parameter

$$\tilde{T} = \frac{\int_{\sigma_m \rho^{1/3}}^{\xi_C} |g(\xi) - 1| d\xi}{\xi_C - \sigma_m \rho^{1/3}}$$

Truskett et al PRE 62, 993 (2000)

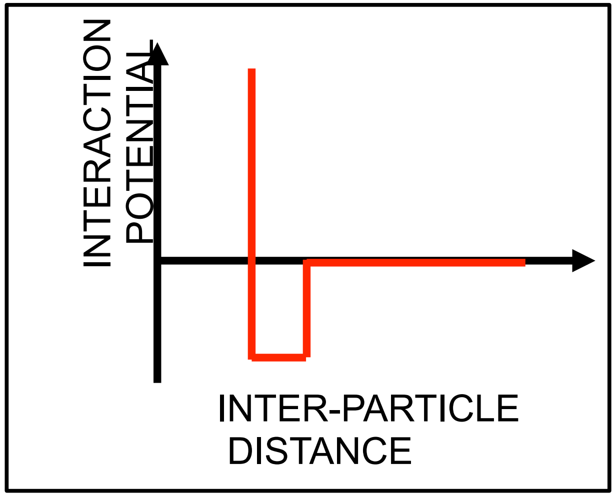
N. Gnan et al in preparation

Depletant model for percolation



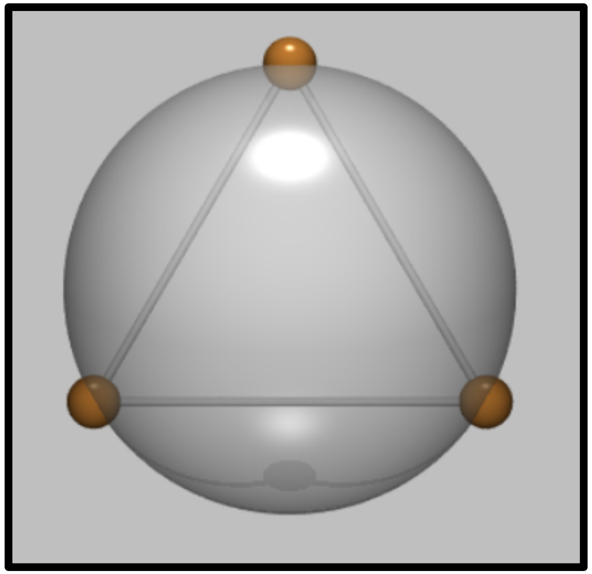
3-patches Kern-Frenkel potential (3P)
Square-well potential (SW)

$$\Phi_{ij}^{3P}(\mathbf{r}_{ij};\hat{n}_i,\hat{n}_j) = \Phi_{ij}^{SW}(r_{ij}) \cdot f(\hat{r}_{ij};\hat{n}_i,\hat{n}_j)$$



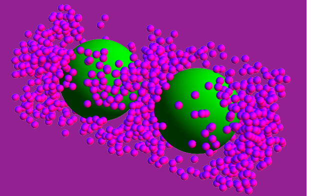
SW potential modulated by an angular function

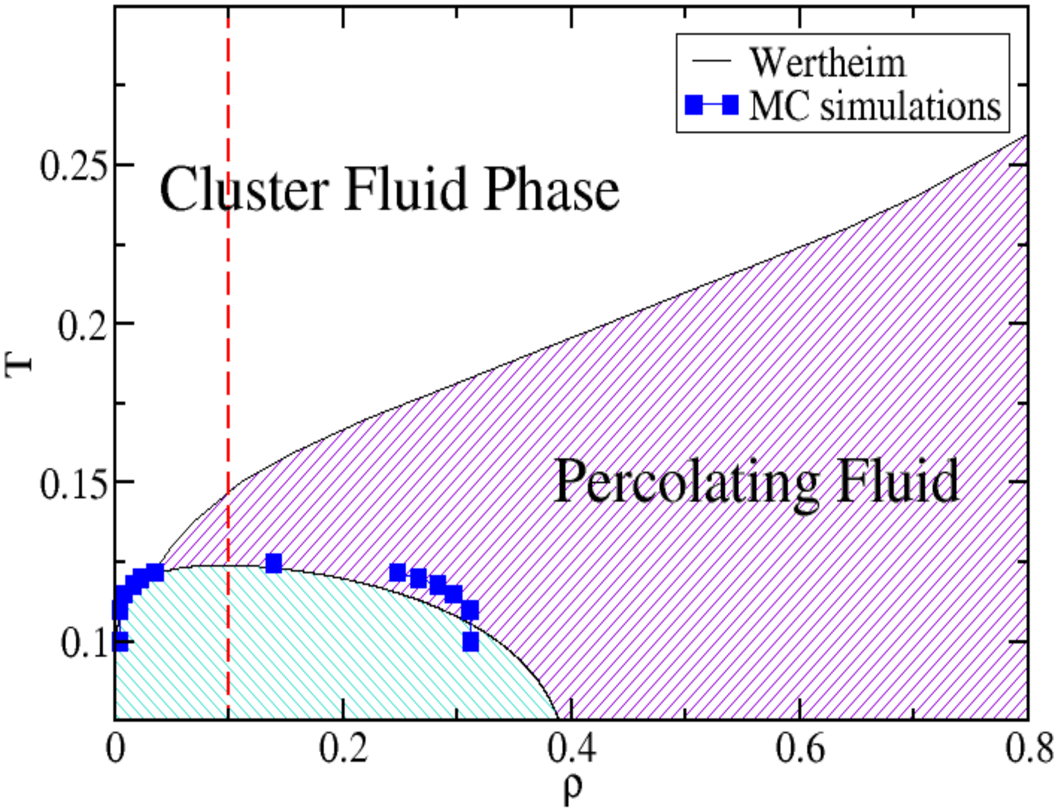
$$\Phi_{ij}^{SW}(r_{ij}) = \begin{cases} \infty, & r < \sigma_s \\ -\varepsilon, & \sigma_s \leq r < (1+\Delta)\sigma_s \\ 0, & r \geq (1+\Delta)\sigma_s \end{cases}$$

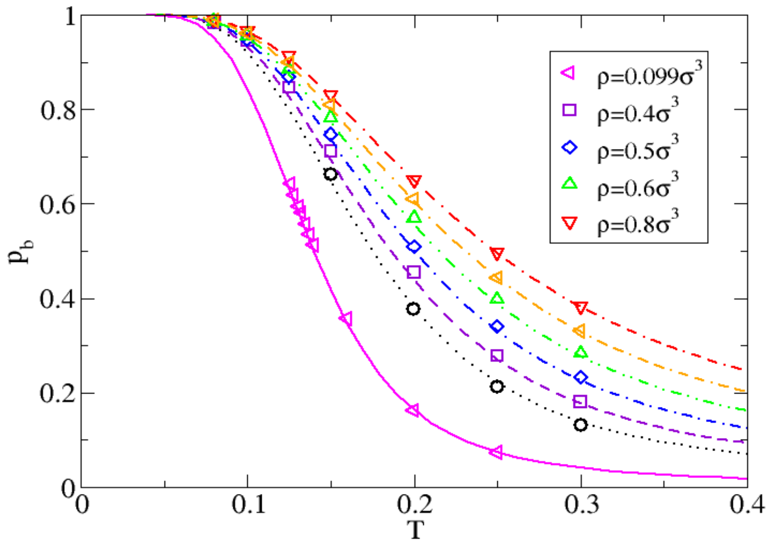


$$f(\hat{r}_{ij};\hat{n}_i,\hat{n}_j) = \begin{cases} 1, & if \begin{cases} if & \hat{r}_{ij} \cdot \hat{n}_i^{(\alpha)} \geq \cos(\theta) \\ and & \hat{r}_{ij} \cdot \hat{n}_j^{(\alpha)} \geq \cos(\theta) \end{cases} \\ 0 & otherwise. \end{cases}$$

How to find the percolation treshold (N=10836)

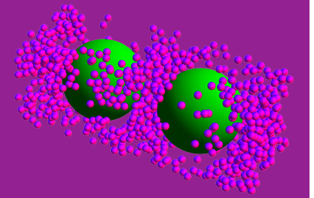


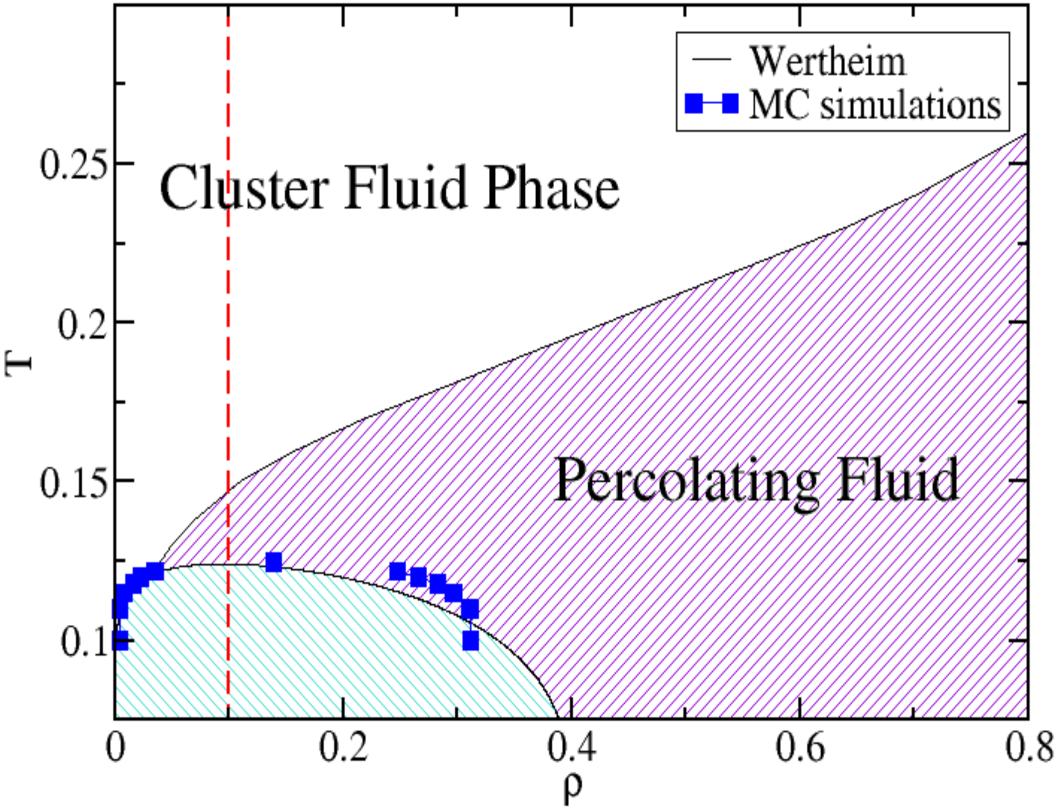




- Evaluate the bond probability for different T

How to find the percolation treshold (N=10836)





- Evaluate the bond probability for different T
- Extrapolate the bond probability at percolation

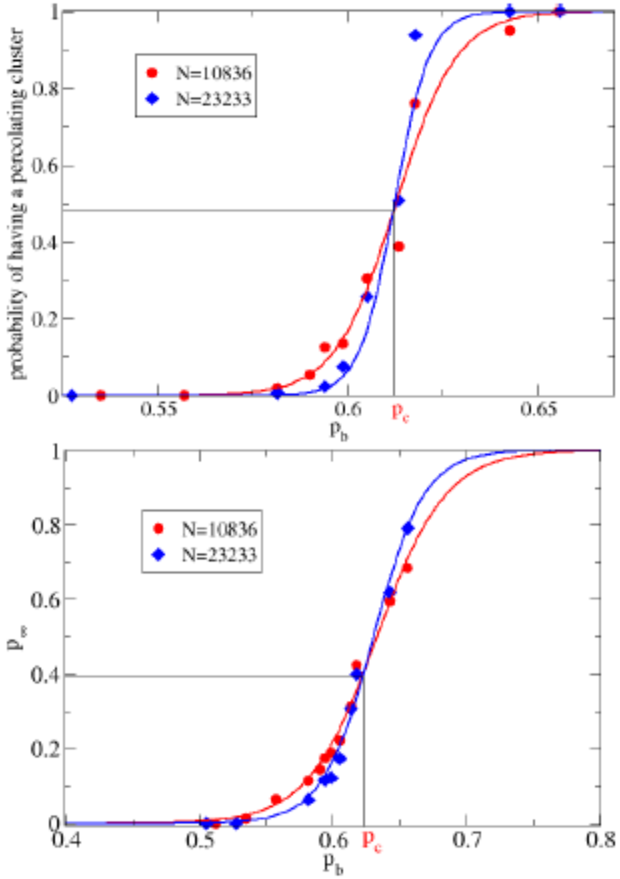
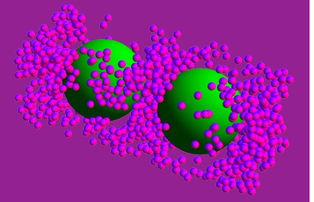
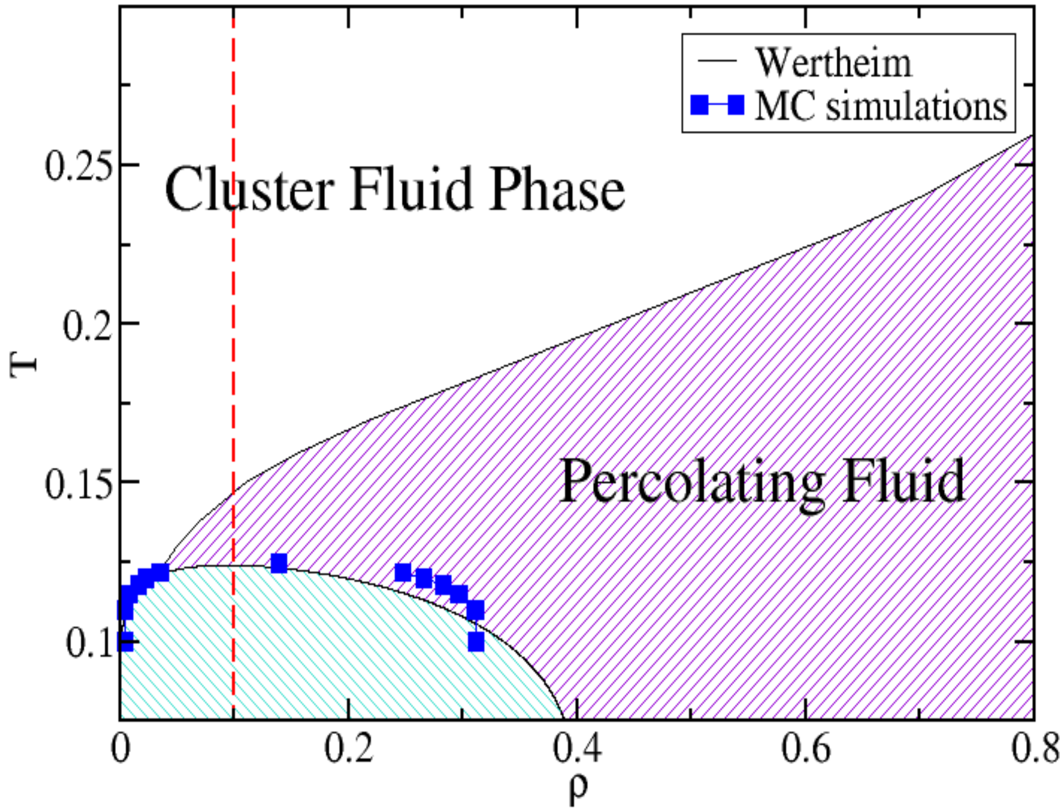
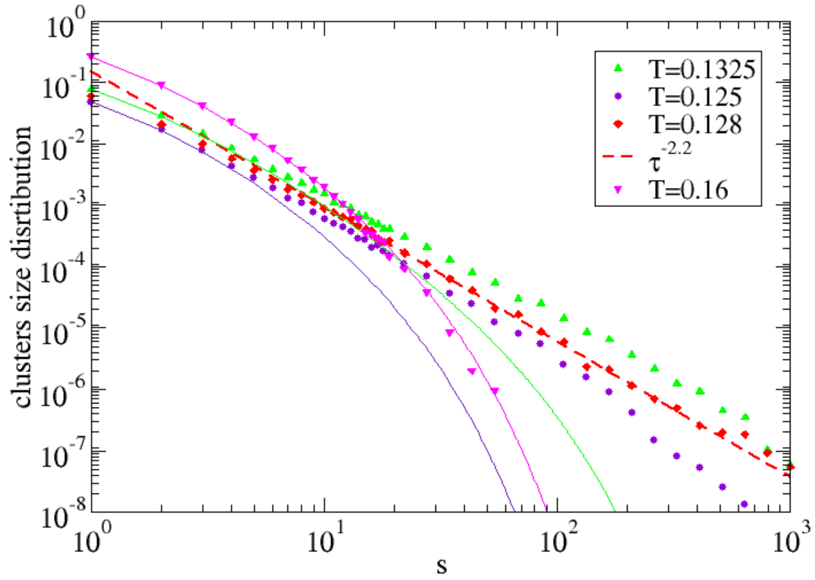


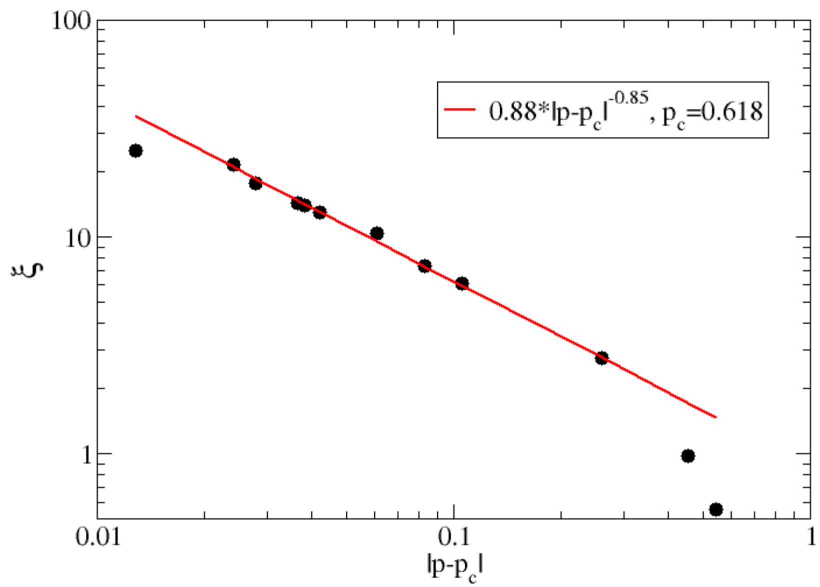
FIG. 7: (a)probability of finding an infinite cluster as a function of p for two sizes of the system.(b)fraction of particles belonging to the infinite cluster p_∞. p_c is roughly estimated as the value of p at which the curves in both figures meet.

How to find the percolation treshold





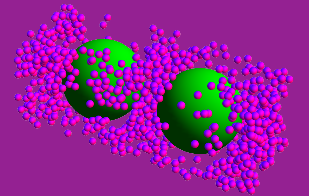




- Check the power-law behavior of the cluster size distribution close to percolation

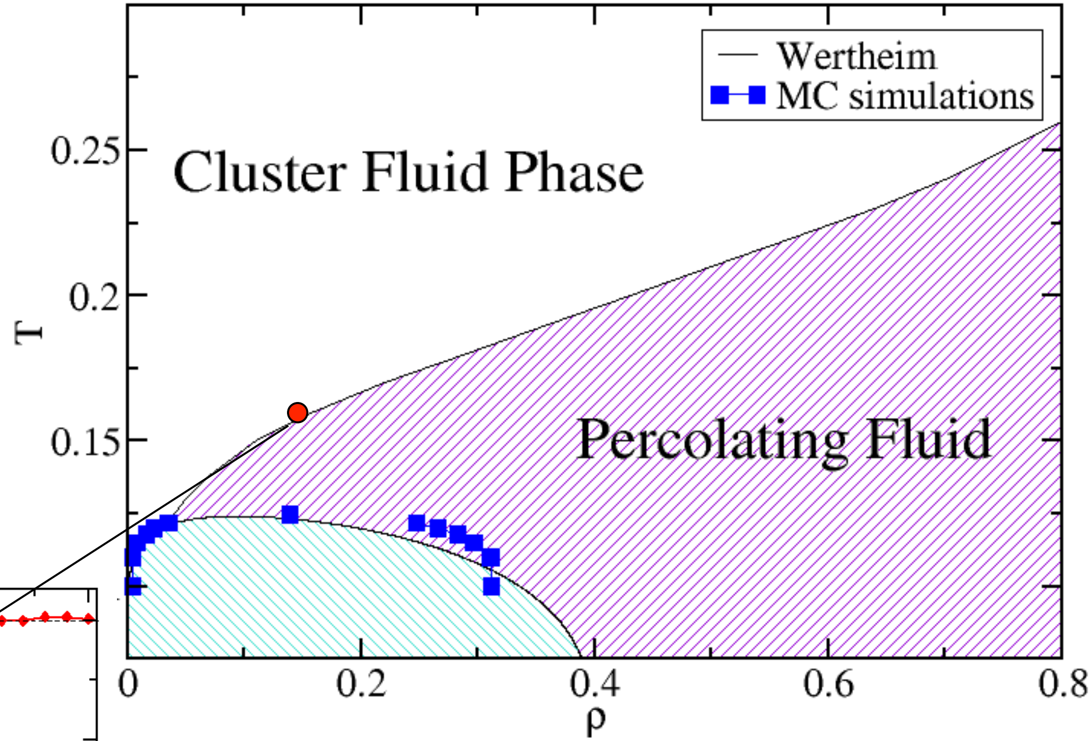
- Check the power-law behavior of the connectivity length close to percolation

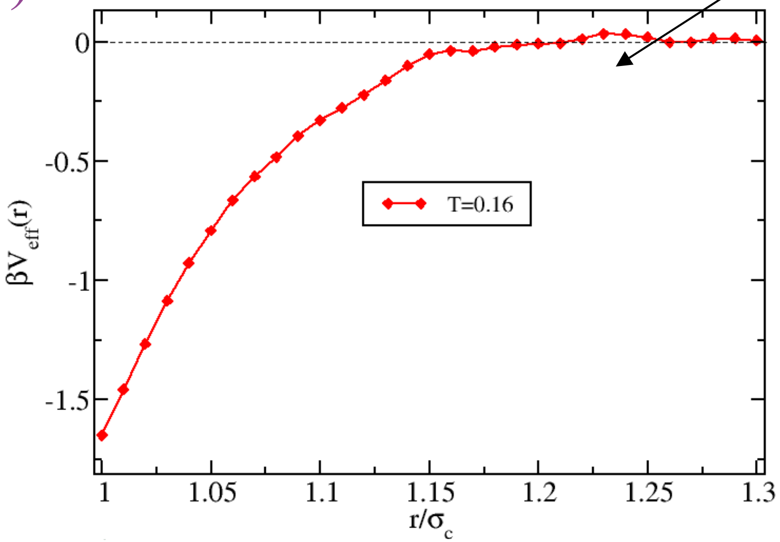
Role of the bond life-time on the potential



- The percolating fluid does not generate long-ranged forces
- An important difference between percolation and cryticality is the non-divergent relaxation time
- This suggests to make the bond life-time very large (infinite)

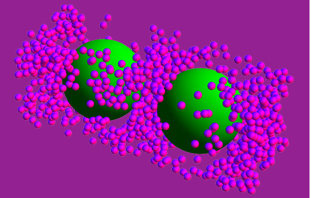
At the critical density just above the percolation line....





There is no diverging long-range behavior in the effective potential

Quantifying the shape of clusters



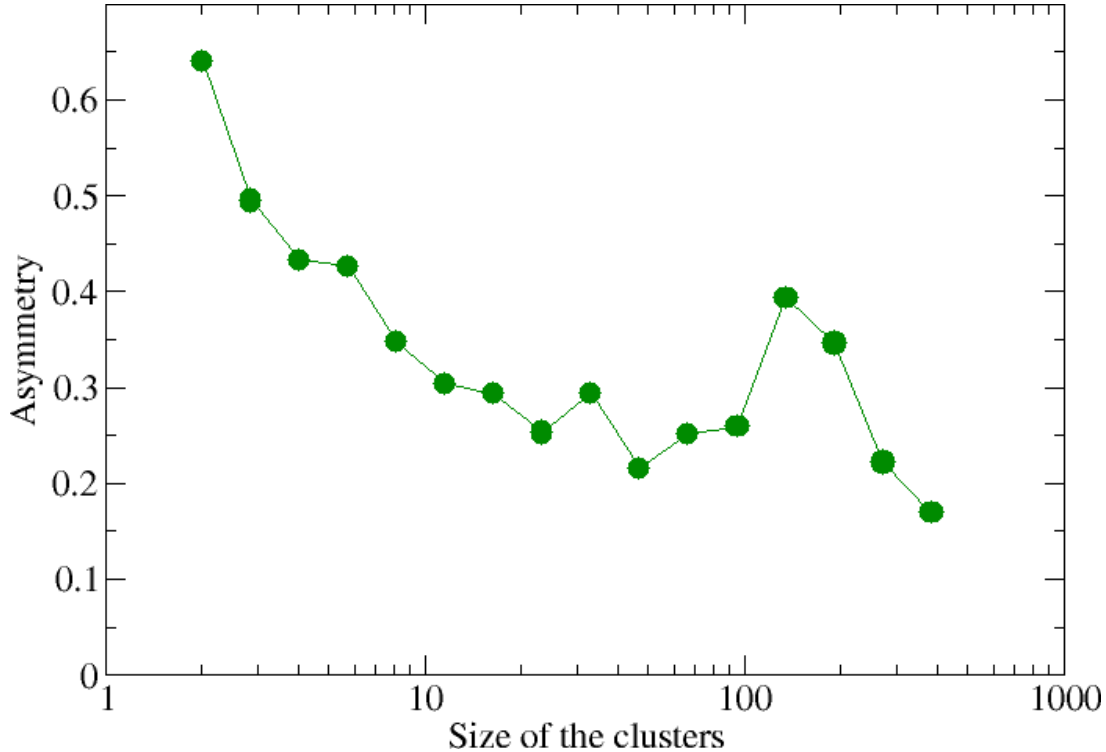
Gyration Tensor

$$\overleftrightarrow{\mathcal{R}} = \begin{pmatrix} \langle x^2 \rangle & \langle xy \rangle & \langle xz \rangle \\ \langle xy \rangle & \langle y^2 \rangle & \langle yz \rangle \\ \langle xz \rangle & \langle yz \rangle & \langle z^2 \rangle \end{pmatrix}$$

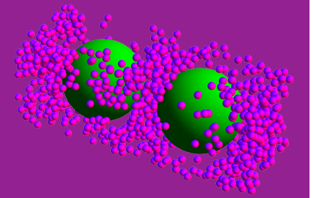
(Displacements from centre of mass)

Asymmetry

$$A_2 = \frac{(\lambda_1 - \lambda_2)^2 + (\lambda_2 - \lambda_3)^2 + (\lambda_3 - \lambda_1)^2}{2(\lambda_1 + \lambda_2 + \lambda_3)^2}$$

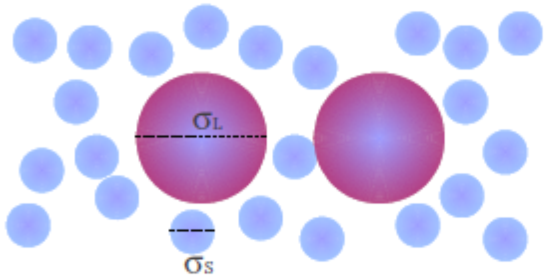


Monte Carlo virtual moves

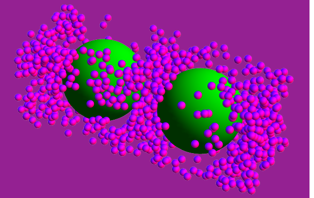


The mean force between two solute molecules at separation r is

$$F(r) = \frac{-\partial A}{\partial r} = k_B T \frac{\partial lnZ}{\partial r}$$



Monte Carlo virtual moves



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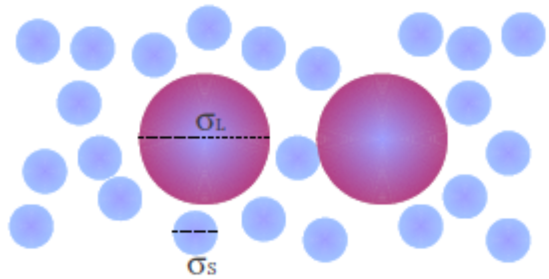
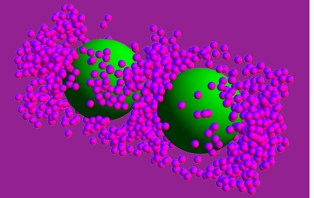


$$F(r) = \frac{-\partial A}{\partial r} = k_B T \frac{\partial lnZ}{\partial r}$$

$$\begin{aligned}
F(r) &= -\frac{k_B T}{Z} \int d\vec{r}_1 \ldots d\vec{r}_N \frac{\partial e^{-\beta \phi_{HS}}}{\partial r} \\
&= \lim_{\Delta r \to 0} -\frac{k_B T}{Z} \int d\vec{r}_1 \ldots d\vec{r}_N e^{-\beta \phi_{HS}(r)} \frac{e^{-\beta \phi_{HS}(r+\Delta r)} - e^{-\beta \phi_{HS}(r)}}{\Delta r} e^{\beta \phi_{HS}(r)} \\
&= \lim_{\Delta r \to 0} -\frac{k_B T}{Z} \int d\vec{r}_1 \ldots d\vec{r}_N \frac{\left[e^{-\beta \Delta \phi_{HS}} - 1\right]}{\Delta r} e^{-\beta \phi_{HS}(r)} \\
&= \lim_{\Delta r \to 0} -\frac{\langle e^{-\beta \Delta \phi_{HS}} - 1 \rangle}{\Delta r}
\end{aligned}$$

Monte Carlo virtual moves



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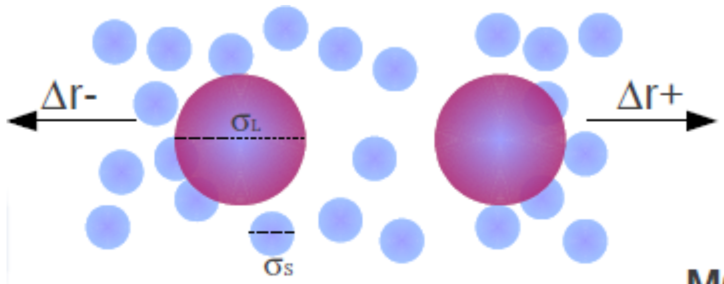

MC Trial Move

$$F(r) = \frac{-\partial A}{\partial r} = k_B T \frac{\partial ln Z}{\partial r}$$

$$\begin{aligned}
F(r) &= -\frac{k_B T}{Z} \int d\vec{r}_1 \ldots d\vec{r}_N \frac{\partial e^{-\beta \phi_{HS}}}{\partial r} \\
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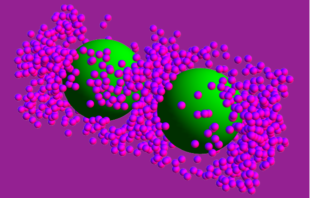
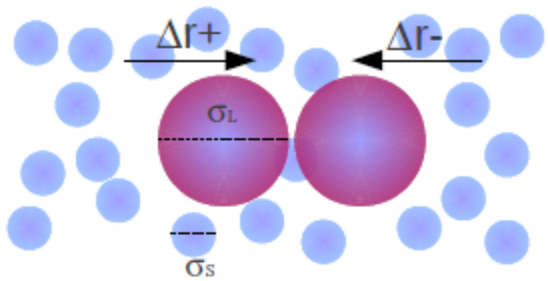
&= \lim_{\Delta r \to 0} -\frac{k_B T}{Z} \int d\vec{r}_1 \ldots d\vec{r}_N \frac{\left[e^{-\beta \Delta \phi_{HS}} - 1\right]}{\Delta r} e^{-\beta \phi_{HS}(r)} \\
&= \lim_{\Delta r \to 0} -\frac{\langle e^{-\beta \Delta \phi_{HS}} - 1 \rangle}{\Delta r}
\end{aligned}$$

Monte Carlo virtual moves



The mean force between two solute molecules at separation r is

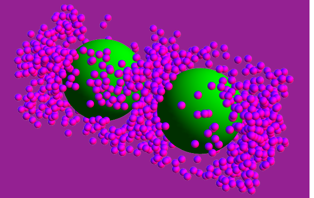
$$F(r) = \frac{-\partial A}{\partial r} = k_B T \frac{\partial ln Z}{\partial r}$$



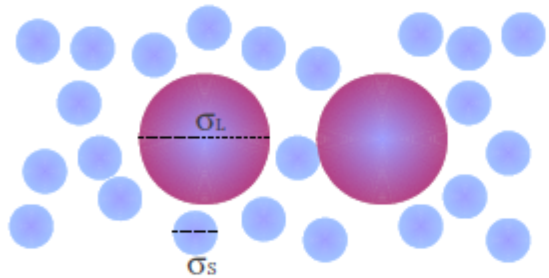
MC Trial Move

$$\begin{aligned}
F(r) &= -\frac{k_B T}{Z} \int d\vec{r}_1 \ldots d\vec{r}_N \frac{\partial e^{-\beta \phi_{HS}}}{\partial r} \\
&= \lim_{\Delta r \to 0} -\frac{k_B T}{Z} \int d\vec{r}_1 \ldots d\vec{r}_N e^{-\beta \phi_{HS}(r)} \frac{e^{-\beta \phi_{HS}(r+\Delta r)} - e^{-\beta \phi_{HS}(r)}}{\Delta r} e^{\beta \phi_{HS}(r)} \\
&= \lim_{\Delta r \to 0} -\frac{k_B T}{Z} \int d\vec{r}_1 \ldots d\vec{r}_N \frac{\left[e^{-\beta \Delta \phi_{HS}} - 1\right]}{\Delta r} e^{-\beta \phi_{HS}(r)} \\
&= \lim_{\Delta r \to 0} -\frac{\langle e^{-\beta \Delta \phi_{HS}} - 1 \rangle}{\Delta r}
\end{aligned}$$

Monte Carlo virtual moves



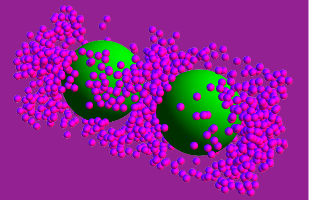
The mean force between two solute molecules at separation r is



$$F(r) = \frac{-\partial A}{\partial r} = k_B T \frac{\partial lnZ}{\partial r}$$

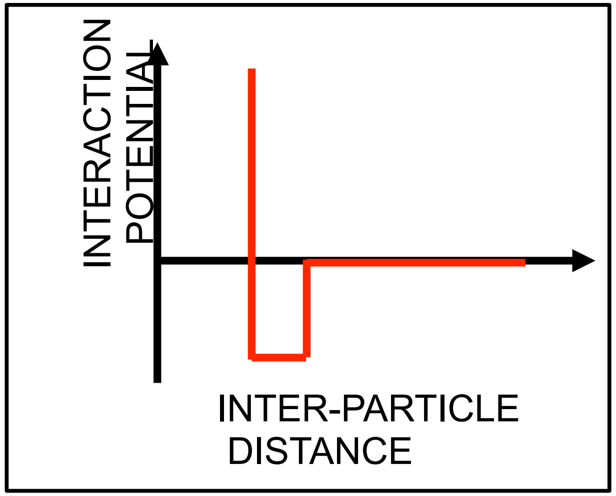
$$\begin{aligned}
F(r) &= -\frac{k_B T}{Z} \int d\vec{r}_1 \ldots d\vec{r}_N \frac{\partial e^{-\beta \phi_{HS}}}{\partial r} \\
&= \lim_{\Delta r \to 0} -\frac{k_B T}{Z} \int d\vec{r}_1 \ldots d\vec{r}_N e^{-\beta \phi_{HS}(r)} \frac{e^{-\beta \phi_{HS}(r+\Delta r)} - e^{-\beta \phi_{HS}(r)}}{\Delta r} e^{\beta \phi_{HS}(r)} \\
&= \lim_{\Delta r \to 0} -\frac{k_B T}{Z} \int d\vec{r}_1 \ldots d\vec{r}_N \frac{\left[e^{-\beta \Delta \phi_{HS}} - 1\right]}{\Delta r} e^{-\beta \phi_{HS}(r)} \\
&= \lim_{\Delta r \to 0^+} -\frac{\langle e^{-\beta \Delta \phi_{HS}} - 1 \rangle}{\Delta r} + \lim_{\Delta r \to 0^-} -\frac{\langle e^{-\beta \Delta \phi_{HS}} - 1 \rangle}{\Delta r}
\end{aligned}$$

Depletant models



Square-well potential (SW)

$$\Phi_{ij}^{SW}(r_{ij}) = \begin{cases} \infty, & r < \sigma_s \\ -\varepsilon, & \sigma_s \leq r < (1+\Delta)\sigma_s \\ 0, & r \geq (1+\Delta)\sigma_s \end{cases}$$

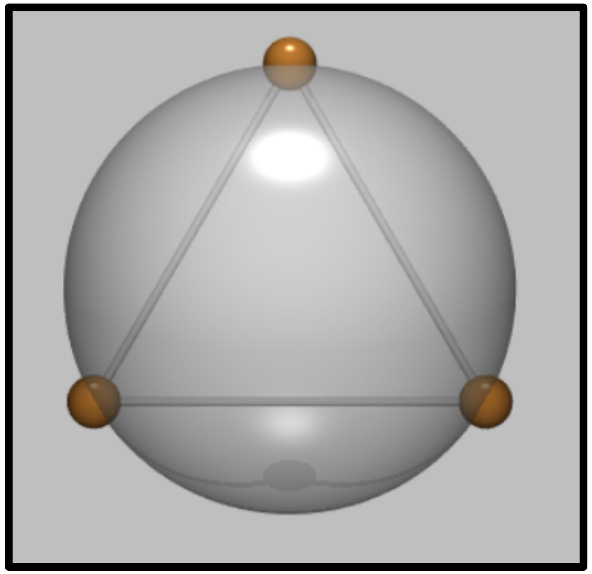


3-patches Kern-Frenkel potential (3P)

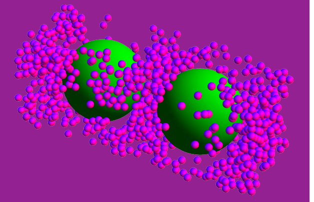
$$\Phi_{ij}^{3P}(\mathbf{r}_{ij};\hat{n}_i,\hat{n}_j) = \Phi_{ij}^{SW}(r_{ij}) \cdot f(\hat{r}_{ij};\hat{n}_i,\hat{n}_j)$$

SW potential modulated by an angular function

$$f(\hat{r}_{ij};\hat{n}_i,\hat{n}_j) = \begin{cases} 1, & if \begin{cases} if & \hat{r}_{ij}\cdot\hat{n}_i^{(\alpha)} \geq \cos(\theta) \\ and & \hat{r}_{ij}\cdot\hat{n}_j^{(\alpha)} \geq \cos(\theta) \end{cases} \\ 0 & otherwise. \end{cases}$$

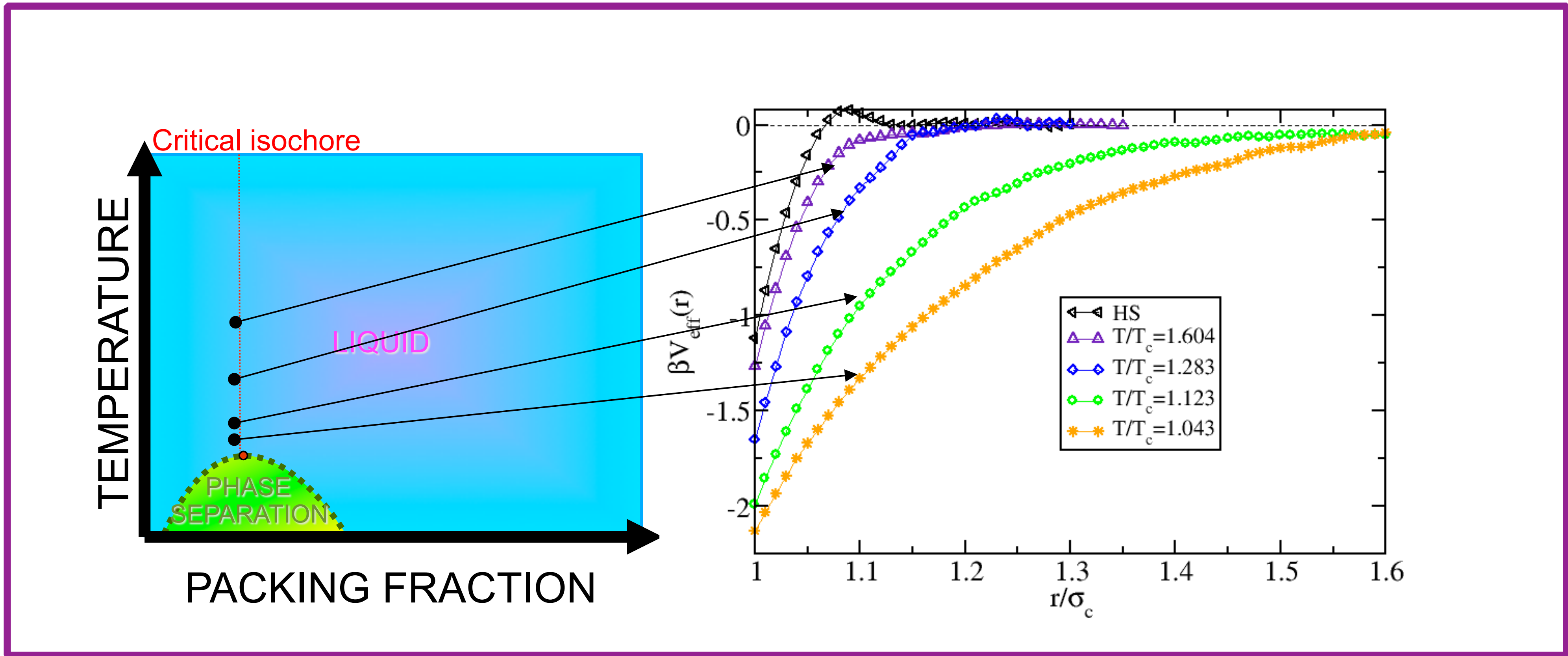


Effective potentials of hard-sphere colloids in two different depletant models



- V_{eff} loses its oscillatory character upon cooling and turns into a **completely attractive** potential

- In addition a progressive significant **increase of the interaction range** is observed on approaching Tc



N. Gnan *et al. Soft Matter 8 (2012),* N. Gnan *et al. JCP 137, 084903 (2012)*