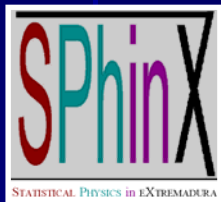


A fluid of penetrable spheres as a model of colloidal solutions of chain polymers. Theory and simulation

Andrés Santos

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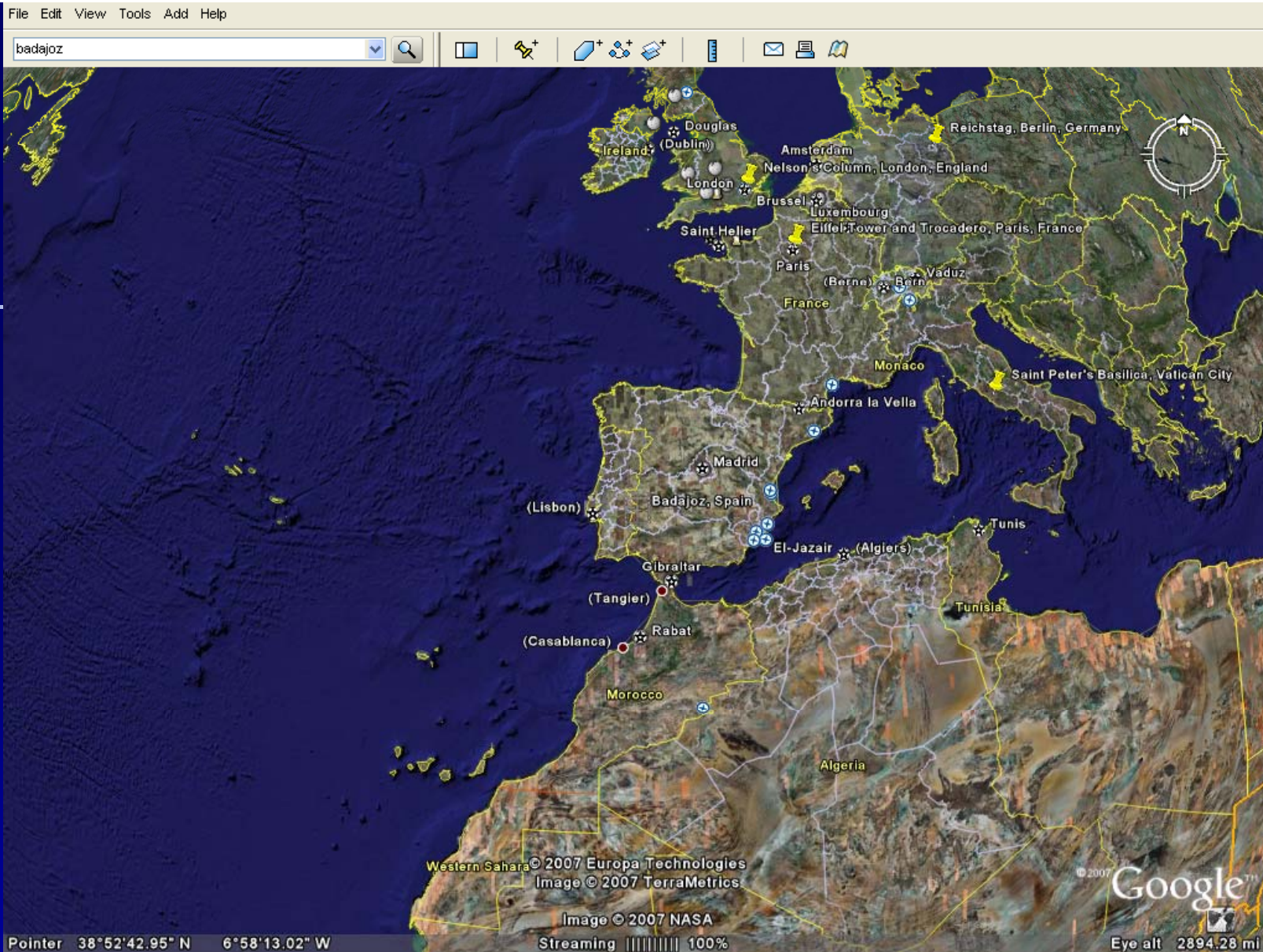


Collaborators:

Luis Acedo (University of Salamanca, Spain)

Alexander Malijevský (Institute of Chemical Technology, Prague, Czech Rep.)

Santos Bravo Yuste (University of Extremadura, Spain)



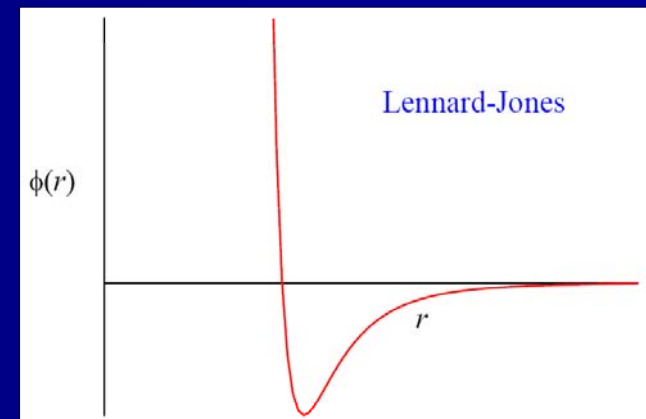
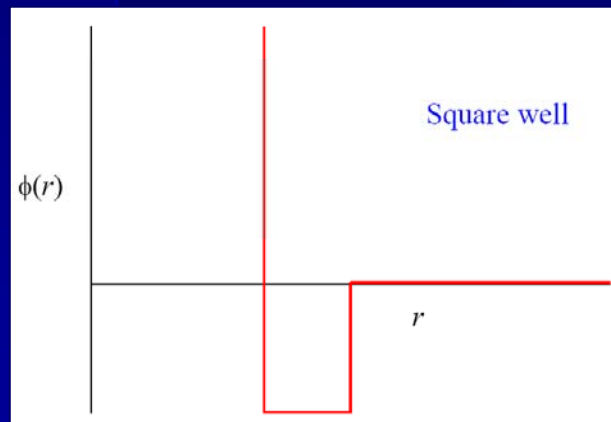
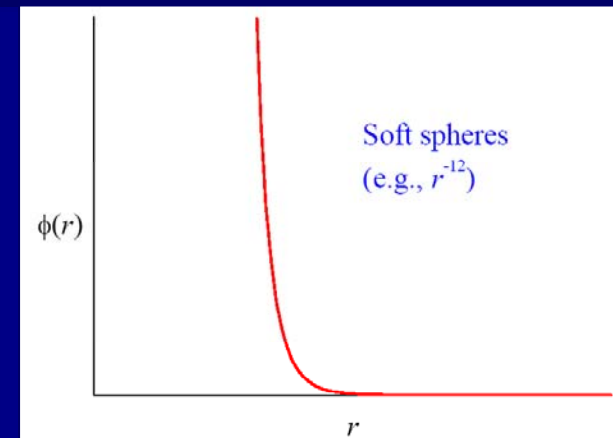
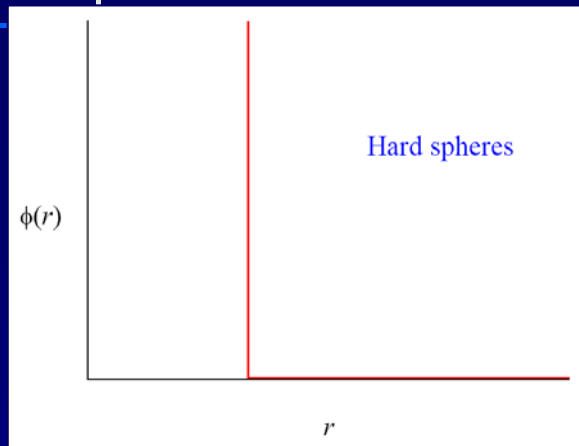
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Traditionally, equilibrium statistical mechanics has been applied to systems made of particles interacting via *unbounded* potentials, e.g.,



In fact, unbounded potentials are useful models to represent the interactions not only in *atomic* systems ($\sigma \approx 1 \text{ \AA} = 0.1 \text{ nm}$), but also in some *colloidal* dispersions ($1 \text{ nm} < \sigma < 1 \text{ }\mu\text{m}$).

For instance, the effective interaction between two sterically stabilized colloidal particles is essentially of hard-sphere (HS) type, perhaps with a short-range attraction (depletion effects).

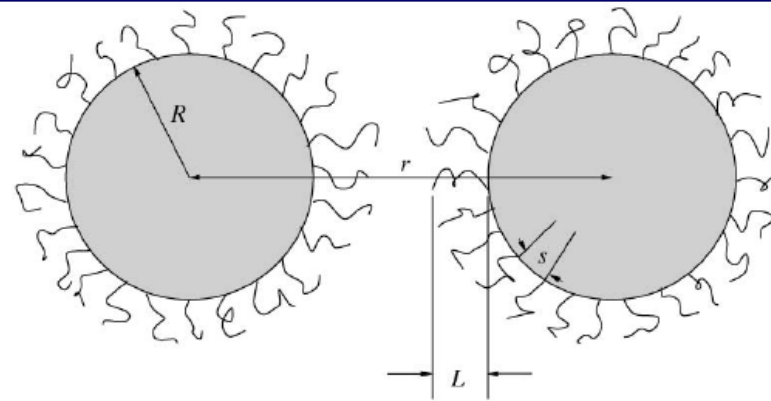


Fig. 4. Two sterically stabilized colloidal particles, each being covered with a polymeric brush whose height is L . The distance between neighboring anchored chains is denoted by s .

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On the other hand, the effective interaction for *star polymers* in good solvents is ultrasoft, logarithmically diverging for short distances.

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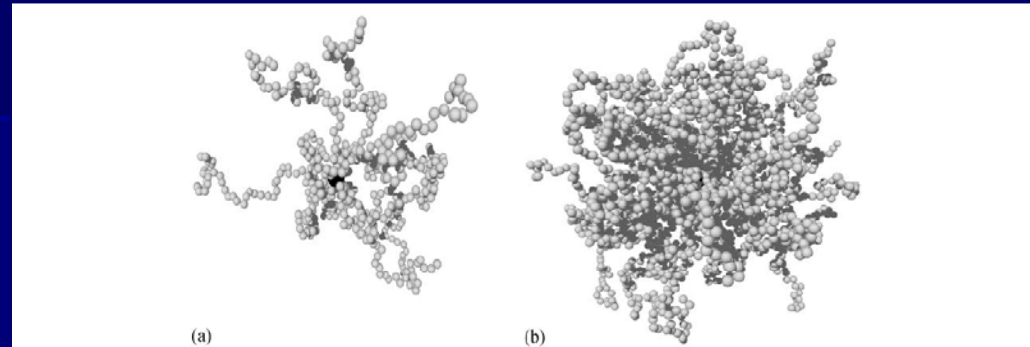


Fig. 37. Snapshots of star polymers in good solvents as obtained from MD simulations employing the model of Grest et al. [330] with: (a) $f = 10$, $N = 50$, and (b) $f = 50$, $N = 50$. For small f , the star looks like a fractal, aspherical object whereas for large f it resembles a spherical colloidal particle. (Taken from Ref. [331].)

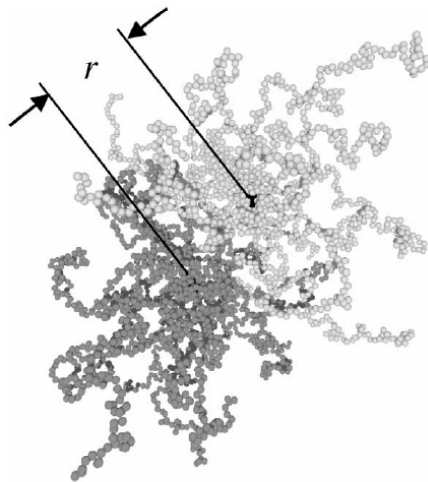


Fig. 42. Typical configuration for two stars with $f = 30$ and $N = 50$, as obtained from a simulation of Ref. [78], with r denoting the distance between their centers. (Courtesy of Ar...

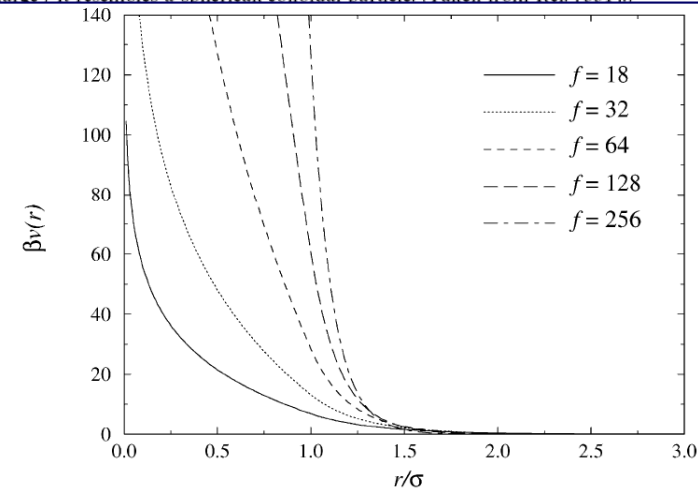


Fig. 40. The effective star-star potential of Eq. (5.57) for a number of different f -values. Notice that the potential becomes harder with increasing f , tending eventually to a HS interaction for $f \rightarrow \infty$.

What about dilute solutions of *polymer chains* in good solvents?

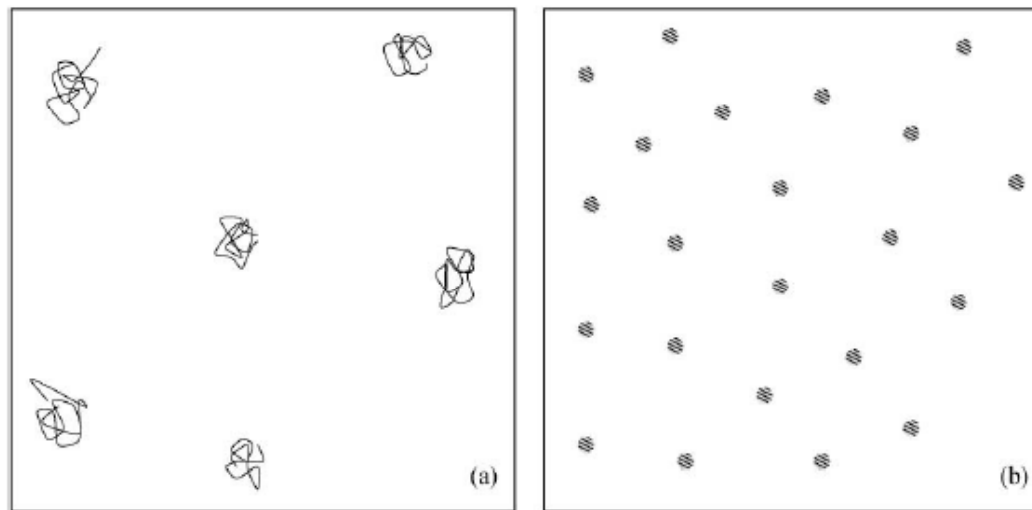


Fig. 13. A dilute polymer solution observed through two different microscopes. In (a) the microscope can resolve details above the monomer length whereas in (b) the microscope can only resolve details above the size of the chain. As a result, all length scales in (b) appear reduced with respect to those in (a) and the objects which appear as flexible chains in (a) show up as “point particles” in (b). Note that the field of view in (b) includes many more particles than in (a).

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Two polymer chains can “sit on top of each other”

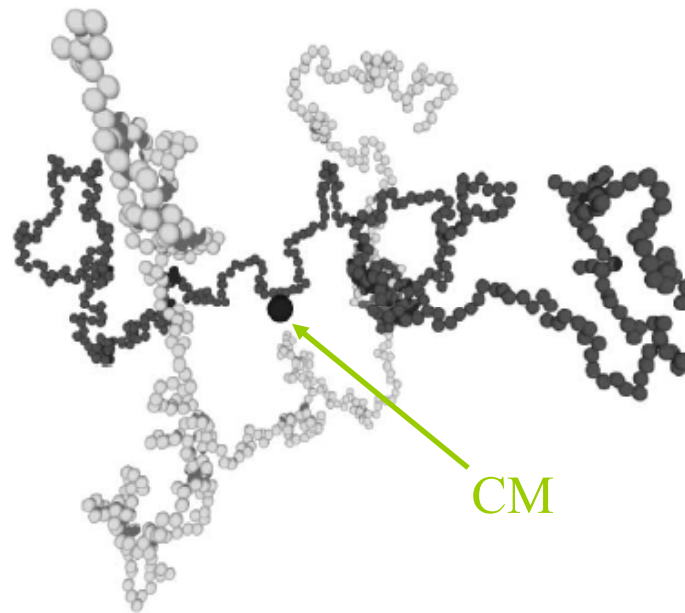
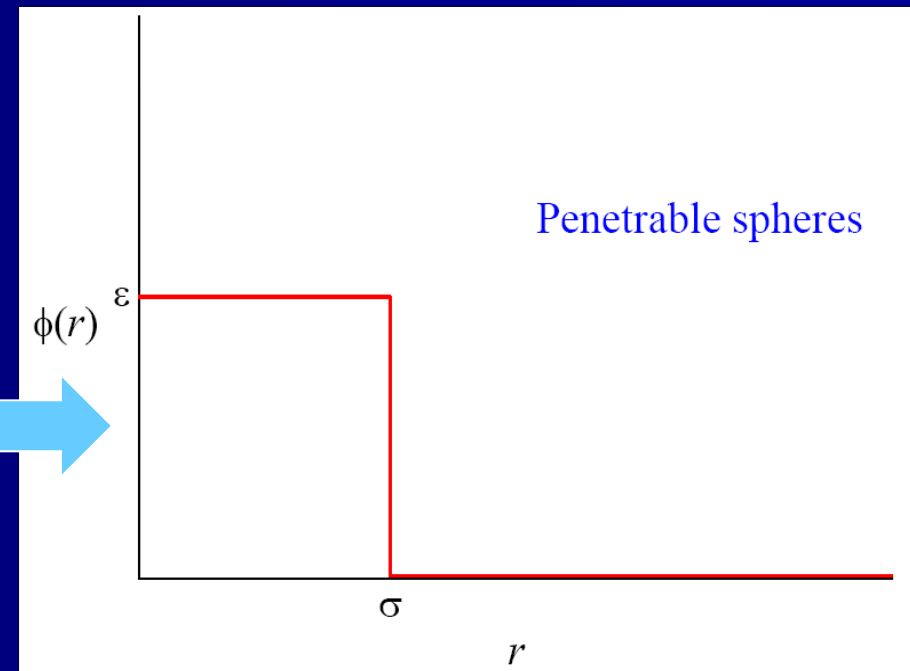
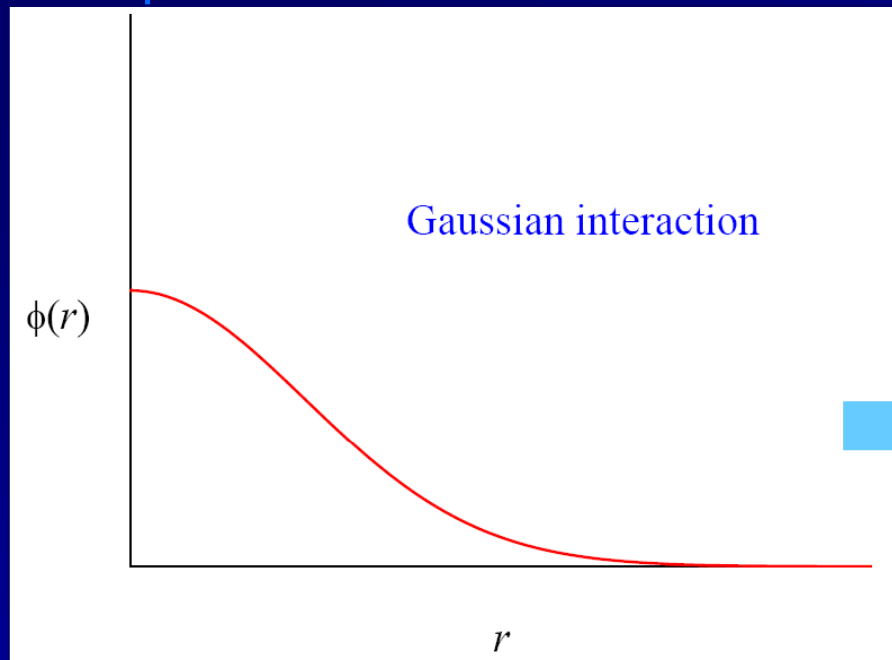


Fig. 14. A snapshot from a simulation involving two self-avoiding polymers. In this configuration, the centers of mass of the two chains (denoted by the big sphere) coincide, without violation of the excluded-volume conditions. (Courtesy of Arben Jusufi.)

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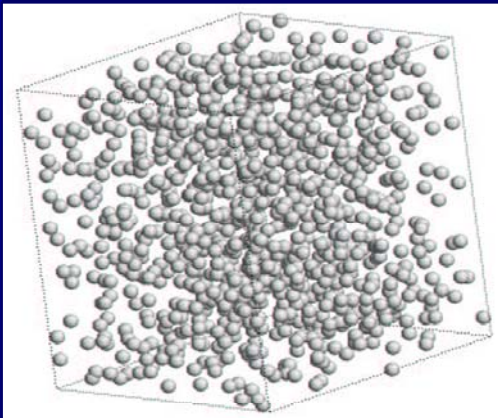
Effective interaction between two polymer chains in a good solvent: *Bounded* potentials, e.g.,



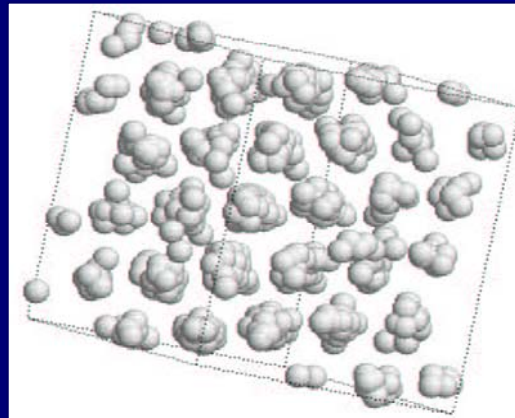
MC simulations (Bianca Mladek, Technische Universität Wien, 2003)

$$T^*=0.5$$

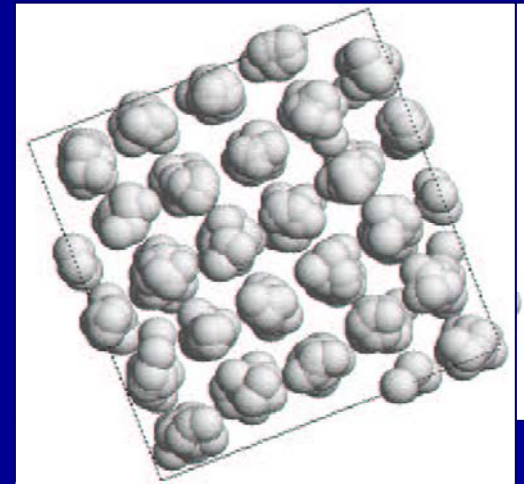
$$\rho\sigma^3=0.5$$



$$\rho\sigma^3=3.5$$



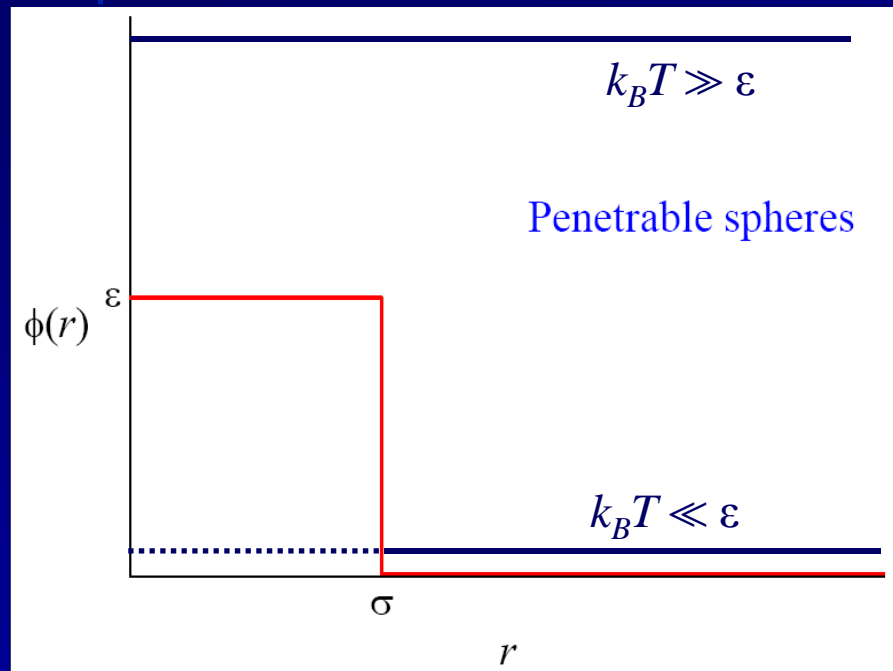
$$\rho\sigma^3=4.0$$



fluid

crystal

Aim: To obtain *analytical* approximations for the (equilibrium) structural properties of a PS fluid and compare with MC simulations



$$T^* \equiv k_B T / \epsilon$$

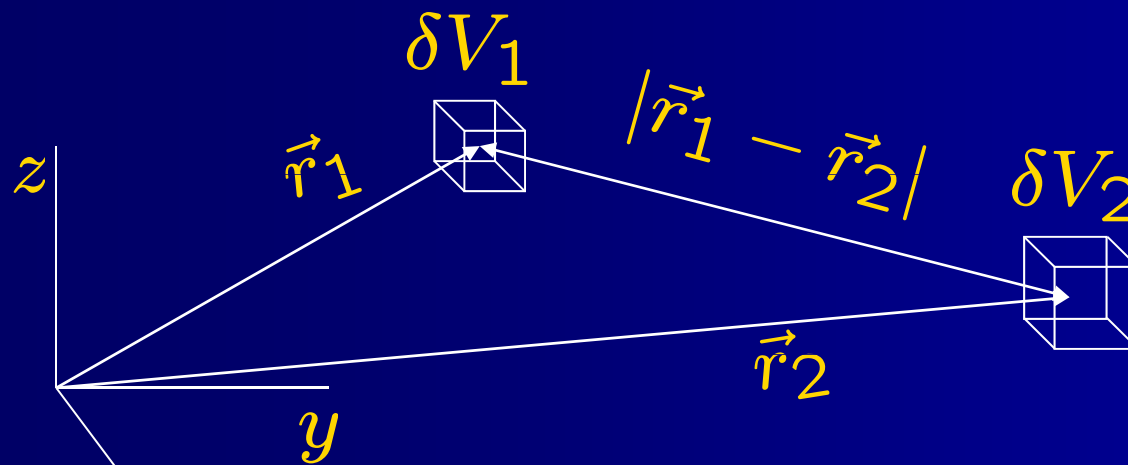
$T^* \rightarrow \infty$: ideal gas
 $T^* \rightarrow 0$: HS fluid

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Pair correlation function or radial distribution function, $g(r)$

$$N_{\text{pairs}}(\vec{r}_1, \vec{r}_2) = \left(\frac{N}{V}\delta V_1\right) \left(\frac{N}{V}\delta V_2\right) g(|\vec{r}_1 - \vec{r}_2|)$$



Quantities related with $g(r)$

$\rho_2(\vec{r}_1, \vec{r}_2) = \rho^2 g(|\vec{r}_1 - \vec{r}_2|)$; $g(r)$: radial distribution function

$y(r) = e^{\phi(r)/k_B T} g(r)$: cavity function

$h(r) = g(r) - 1$: total correlation function

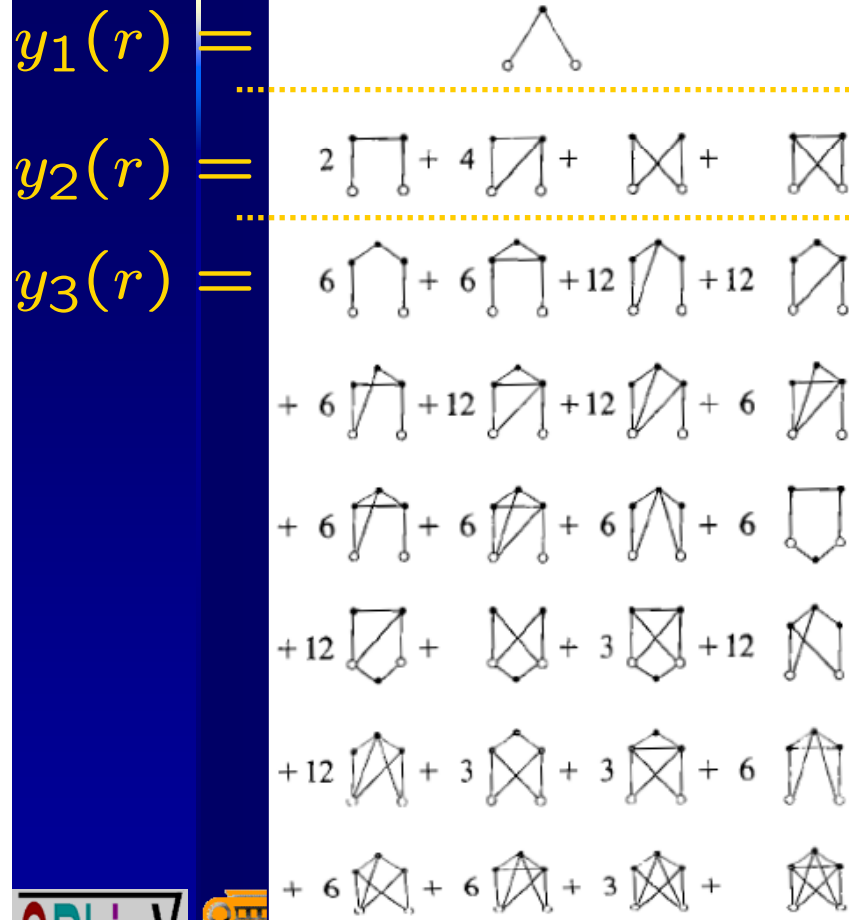
$c(r)$: direct correlation function

$\tilde{c}(k) = \frac{\tilde{h}(k)}{1 + \rho \tilde{h}(k)}$: Ornstein–Zernike relation

$S(k) = 1 + \rho \tilde{h}(k)$: structure factor

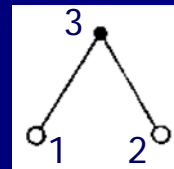
Expansion of the radial distribution function in powers of density:

$$y(r) \equiv e^{\phi(r)/k_B T} g(r) = 1 + \sum_{n=1}^{\infty} \frac{\rho^n}{n!} y_n(r)$$

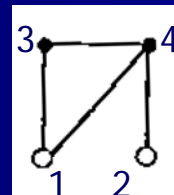


$$f(r) = e^{-\phi(r)/k_B T} - 1$$

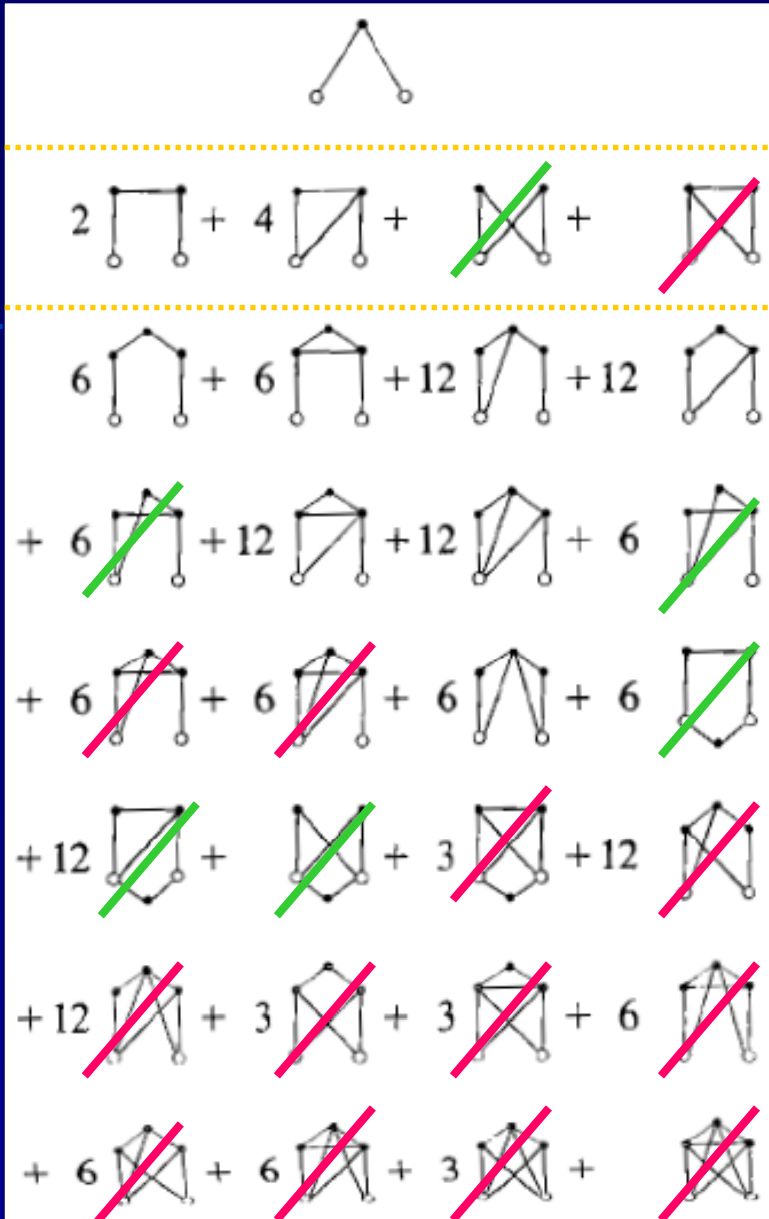
Mayer function



$$= \int dr_3 f(r_{13}) f(r_{23})$$



$$= \int dr_3 \int dr_4 f(r_{13}) f(r_{34}) \times f(r_{24}) f(r_{14})$$



HNC closure:

$$c(r) = g(r) - 1 - \ln y(r)$$

"Elementary" diagrams neglected

Percus–Yevick (PY) closure:

$$c(r) = f(r)y(r)$$

"Elementary" and "Bundle" diagrams neglected

Outline

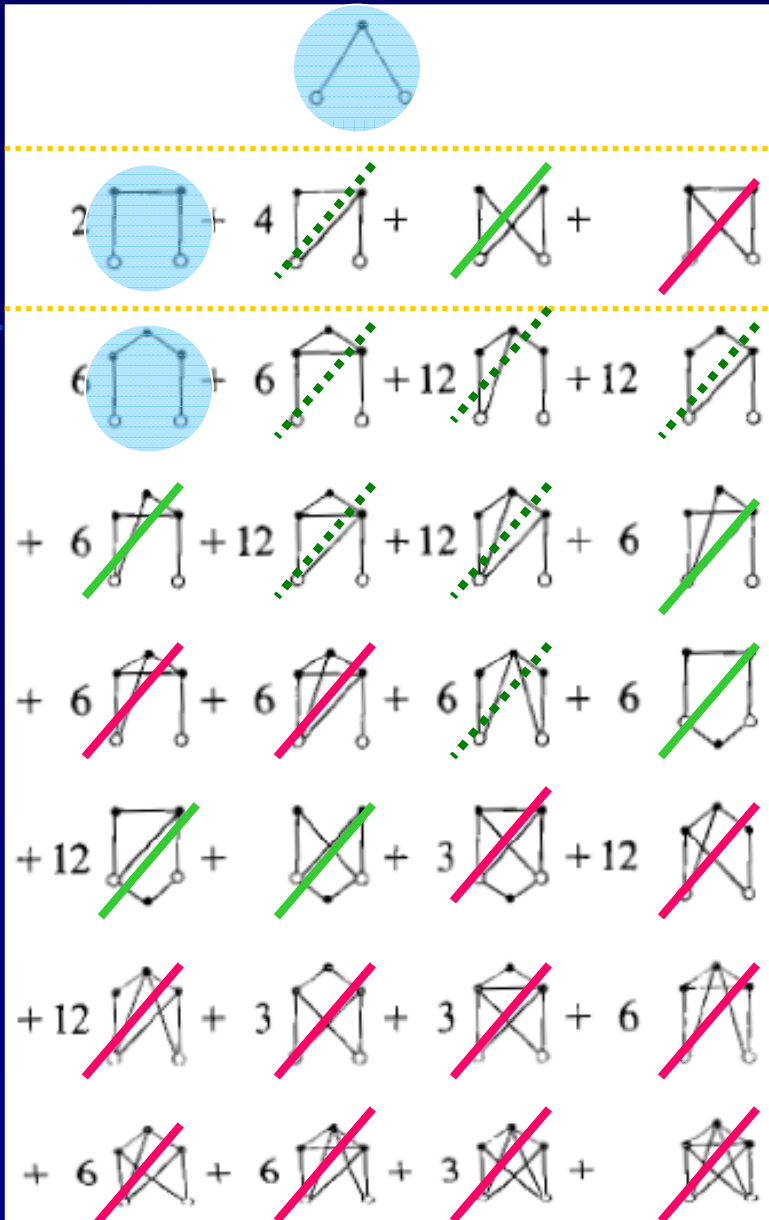
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Mayer function of the PS model

$$f_{\text{PS}}(r) = x f_{\text{HS}}(r), \quad x \equiv 1 - e^{-1/T^*}$$

$$f_{\text{HS}}(r) = \begin{cases} -1, & r < \sigma \\ 0, & r > \sigma \end{cases}$$

The PS model in the high-temperature, high-density limit



$$T^* \rightarrow \infty \Rightarrow x \approx T^{*-1} \rightarrow 0$$

$$\rho \rightarrow \infty, \hat{\rho} \equiv \rho x = \text{finite}$$

Only "chain" diagrams survive!

Spinodal instability

$$S(k) = \frac{1}{1 - \hat{\rho} \tilde{f}_{\text{HS}}(k)}$$

$$\tilde{f}_{\text{HS}}(k) = \tilde{f}_{\text{max}} \text{ at } k = k_0$$

$$S(k_0) \rightarrow \infty \text{ when } \hat{\rho} \rightarrow \hat{\rho}_0 \equiv 1/\tilde{f}_{\text{max}}$$

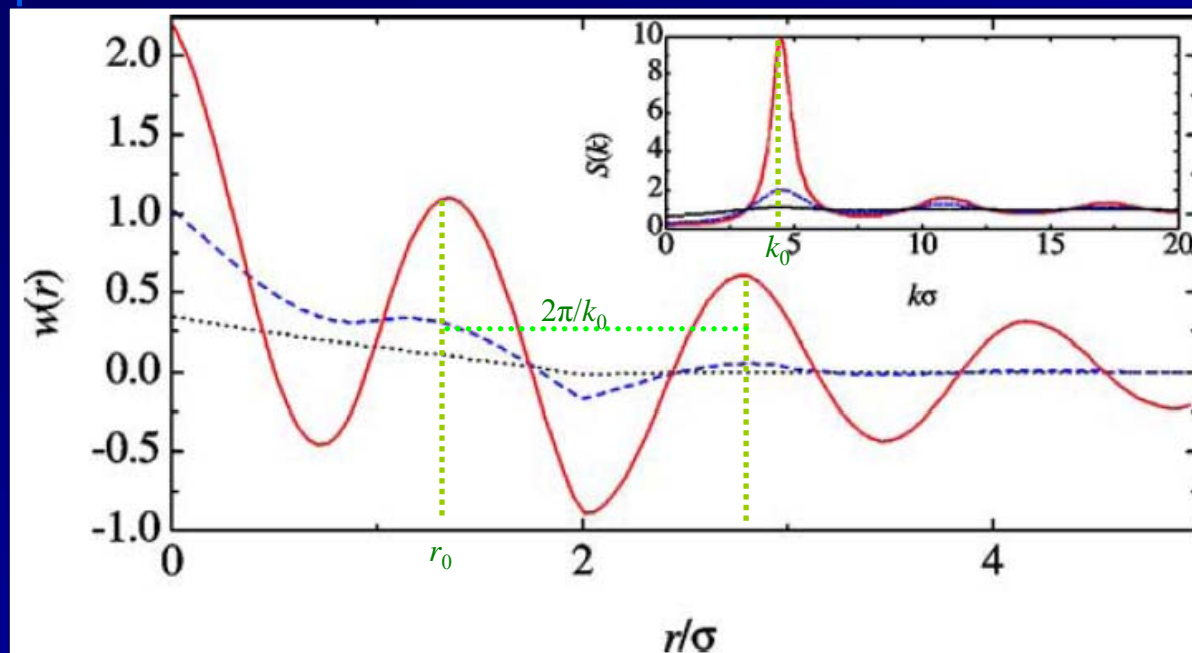


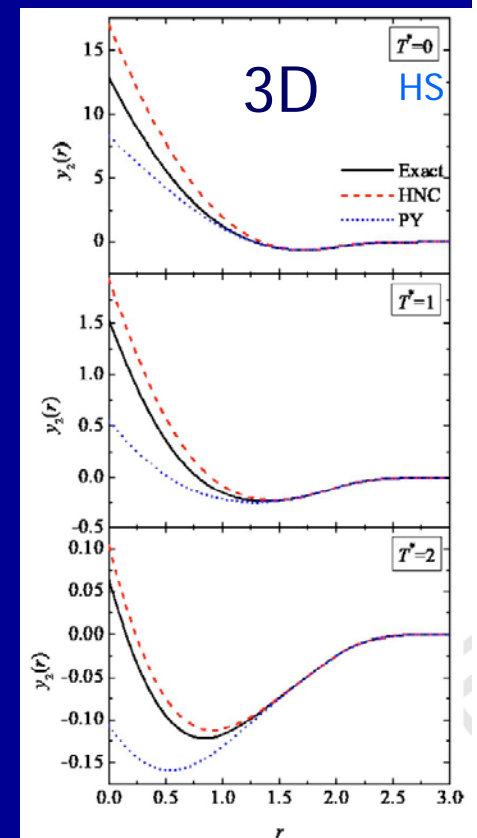
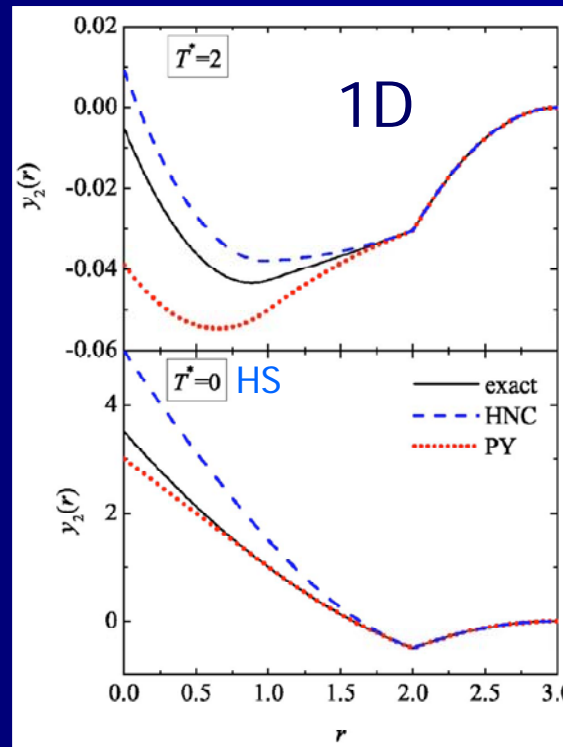
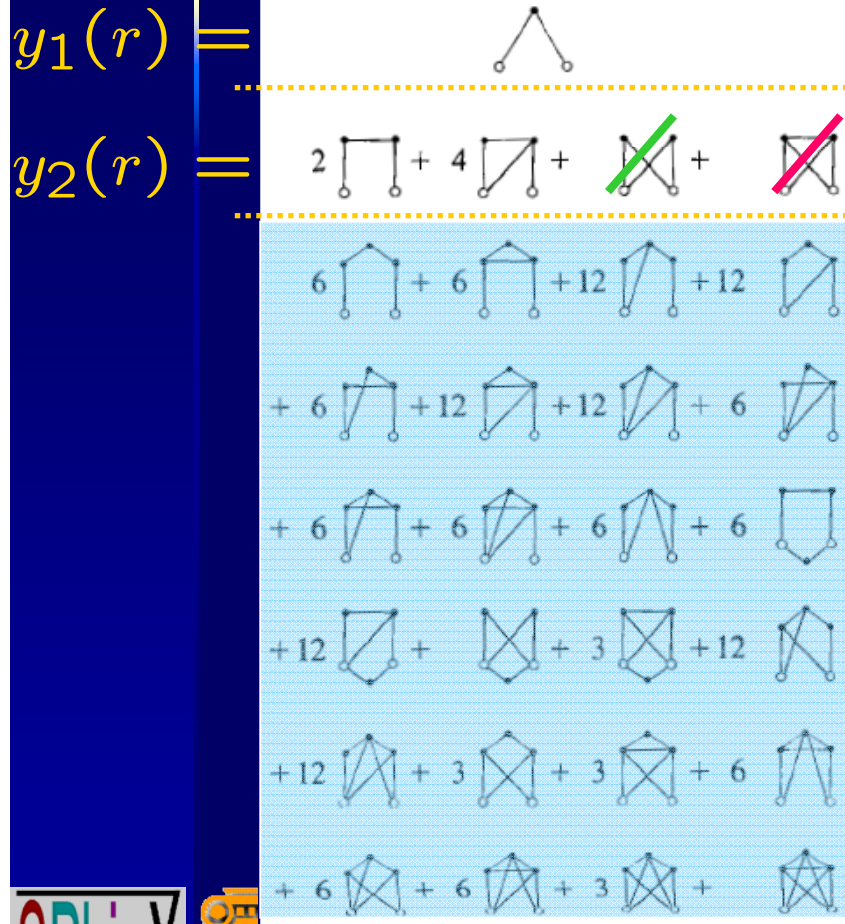
Fig. 2. Plot of $w(r)$ and $S(k)$ (see inset) at $\hat{\eta}/\hat{\eta}_0 = 0.1$ (dotted lines), 0.5 (dashed lines) and 0.9 (solid lines) for $d = 1$.

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Exact behavior to second order in density

$$y(r) \equiv e^{\phi(r)/k_B T} g(r) = 1 + \sum_{n=1}^{\infty} \frac{\rho^n}{n!} y_n(r)$$



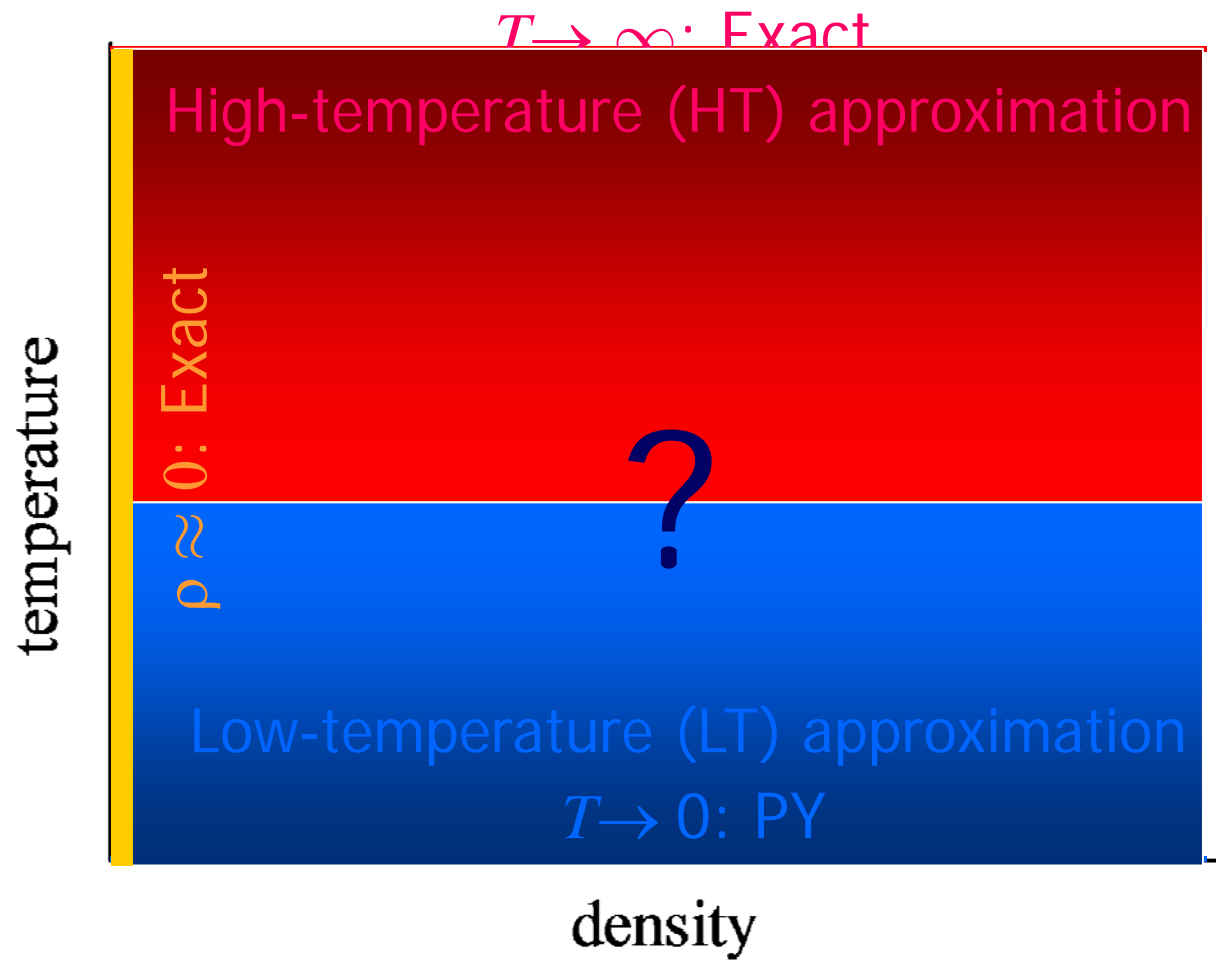
Al. Malijevský and A. Santos

J. Chem. Phys. **124**, 074508 (2006)

PHYSICAL REVIEW E **75**, 021201 (2007)

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High-temperature (HT) approximation

[Al. Malijevský, S. B. Yuste, A.S., preprint 0705.1069]

$$\lim_{\substack{x \rightarrow 0 \\ \rho \rightarrow \infty \\ \hat{\rho} = \rho x}} y(r) = 1 + xw(r), \quad x \equiv 1 - e^{-1/T^*}$$

$$\text{HT: } \boxed{y(r) = 1 + xw(r)e^{xw(r)}}$$

$$g(r) = \begin{cases} (1 - x)y(r), & r < \sigma \\ y(r), & r > \sigma \end{cases}$$

Low-temperature (LT) approximation

[Al. Malijevský, S. B. Yuste, A.S., preprint 0705.1069]

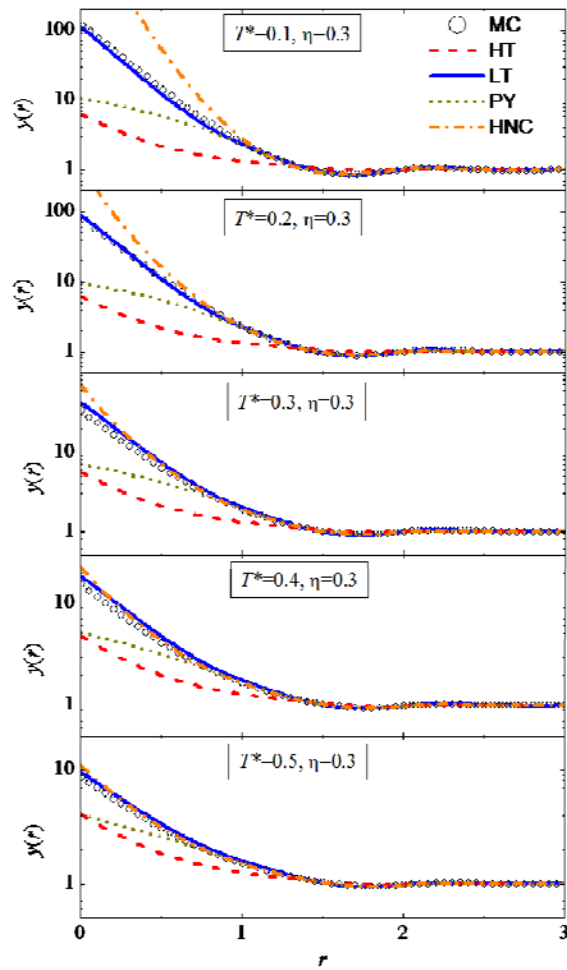
$$g(r) = \frac{e^{Q(r)\Theta(1-r)}}{r} \sum_{n=0}^{\infty} f_n(r-n)\Theta(r-n)$$

$$Q(r) = (r-1) [A + B(r+2)(r-1) + Cr(r-1)]$$

$$f_n(r) = -\mathcal{L}^{-1} \left\{ \frac{t (1 + S_1 t + S_2 t^2 + S_3 t^3) (L_0 + L_1 t)^n}{12\eta (L_0 + S_1 t + S_2 t^2 + S_3 t^3)^{n+1}} \right\}$$

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PHYSICAL REVIEW E VOLUME 58, NUMBER 3 SEPTEMBER 1998
Freezing and clustering transitions for penetrable spheres
 C. N. Likos,¹ M. Watzlawek,² and H. Löwen^{1,2}

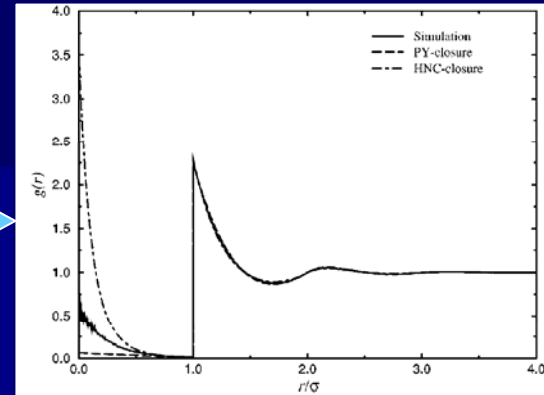
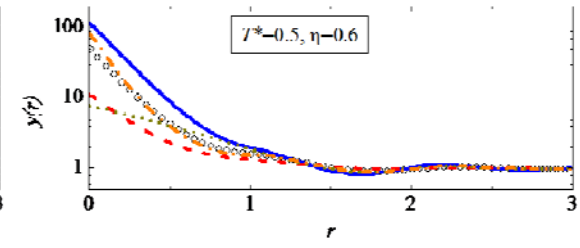
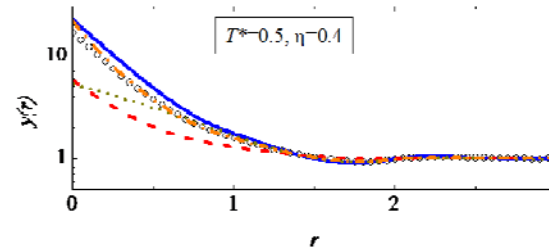
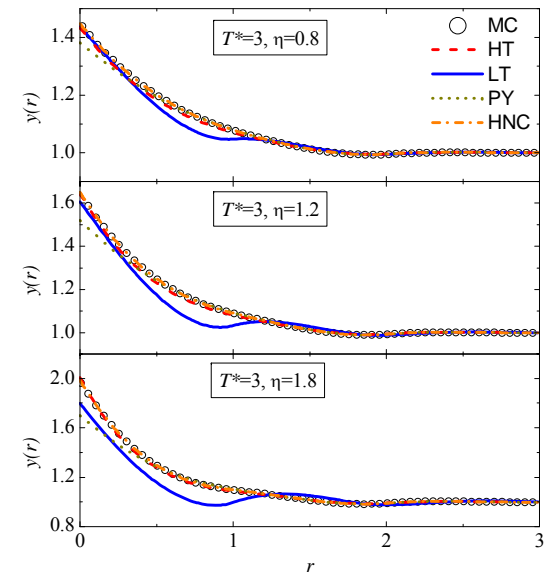
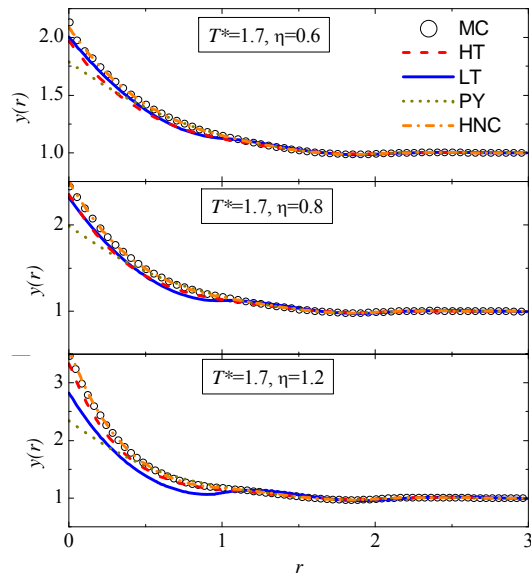
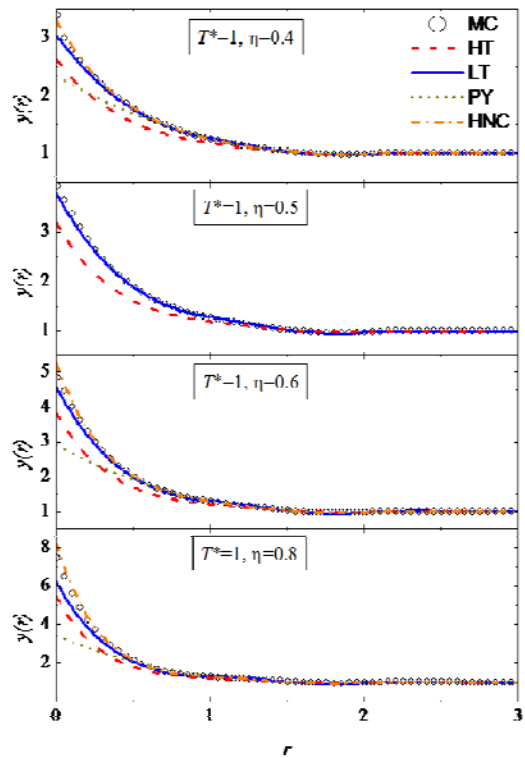
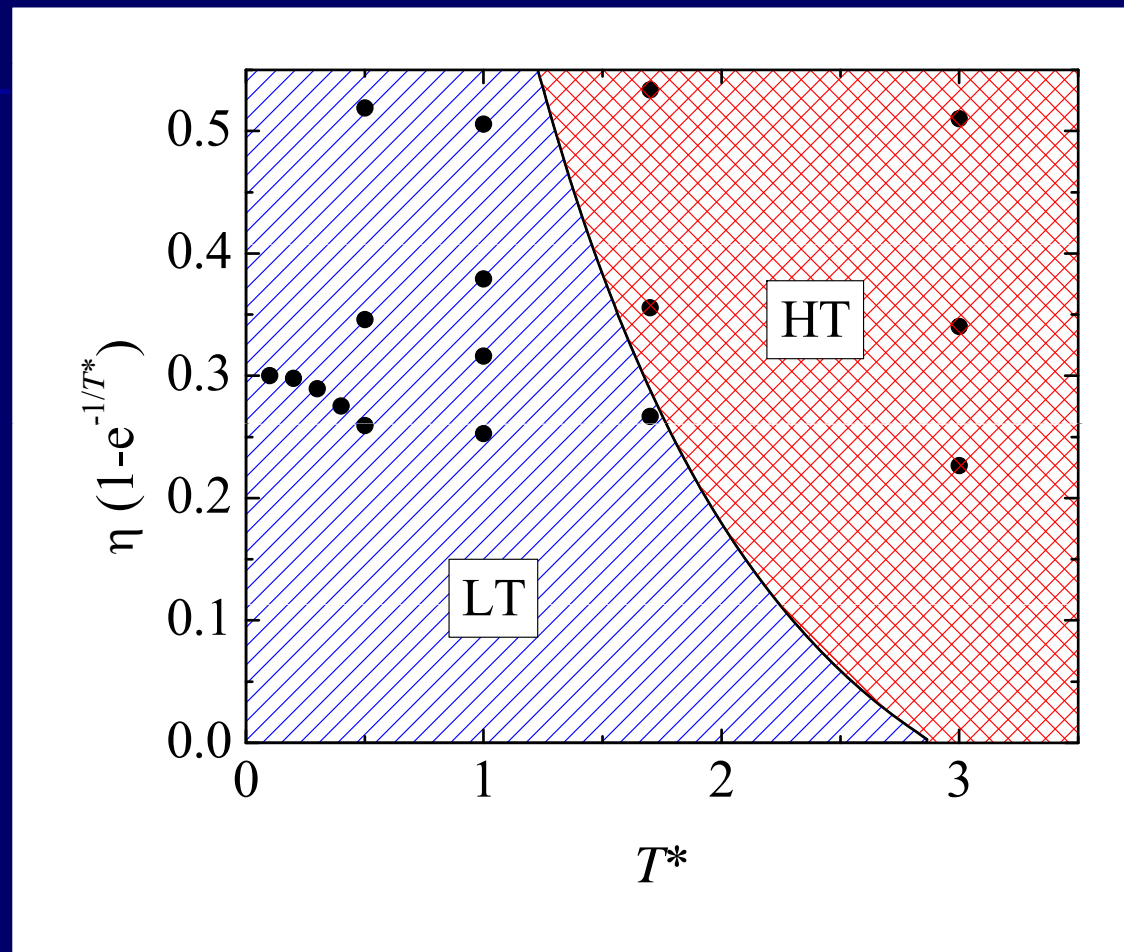


FIG. 1. Comparison of the radial distribution function $g(r)$ as obtained from simulation, and the PY and HNC closures, for a system of penetrable spheres at reduced temperature $t=0.2$ and packing fraction $\eta=0.3$.





"Domains" of the HT and LT approximations



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- The PS model allows one to describe the effective interaction in some soft matter systems, such as colloidal solutions of chain polymers.
- The model is also interesting from a theoretical point of view. It includes the HS fluid ($T^* \rightarrow 0$) and the ideal gas ($T^* \rightarrow \infty$) as particular cases.
- It can be *exactly* solved in the combined limit of high temperatures and densities (mean-field theory).
- By an extrapolation of those exact results, we have constructed an *analytical* theory describing high-temperature (HT) states.

- Starting from the analytical solution of the PY closure for HS, we have constructed an *analytical* theory describing low-temperature (LT) states.
- The LT theory compares well with MC simulation if $T^* \lesssim 1$. The HT theory does it if $T^* \gtrsim 3$.
- The HNC closure provides excellent results, except for $T^* \lesssim 0.3$, while the PY closure is always rather poor in the overlapping region.

Thank you for your attention!

