Structural properties of penetrable-rod fluids. A comparison between Monte Carlo simulations and two simple theories

Andrés Santos

University of Extremadura, Badajoz, Spain

Alexander Malijevský

Institute of Chemical Technology, Prague, Czech Republic

VYSOKÁ ŠKOLA CHEMICKO-TECHNOLOGICKÁ V PRAZE

Dilute solution of *polymer chains* in a good solvent

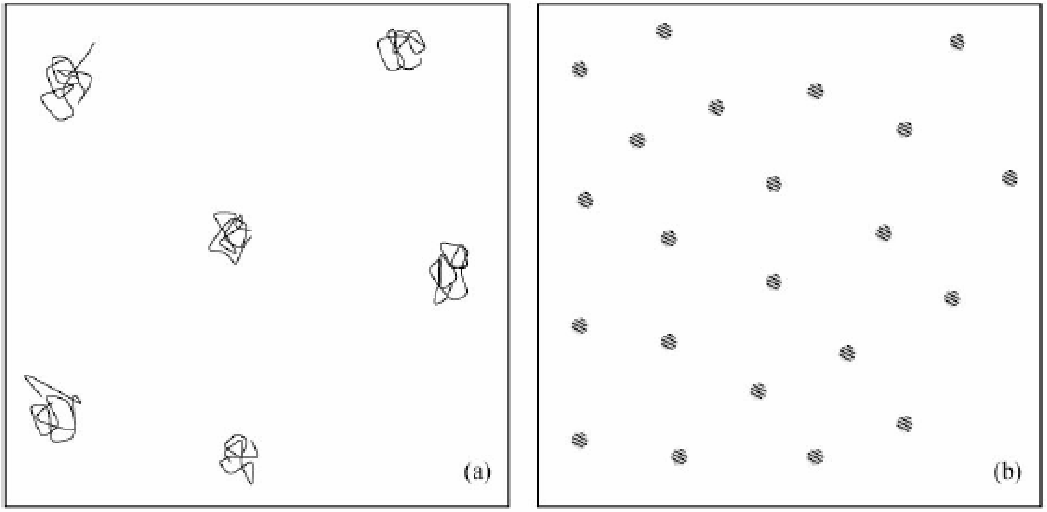


Fig. 13. A dilute polymer solution observed through two different microscopes. In (a) the microscope can resolve details above the monomer length whereas in (b) the microscope can only resolve details above the size of the chain. As a result, all length scales in (b) appear reduced with respect to those 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).

C.N. Likos / Physics Reports 348 (2001) 267–439

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

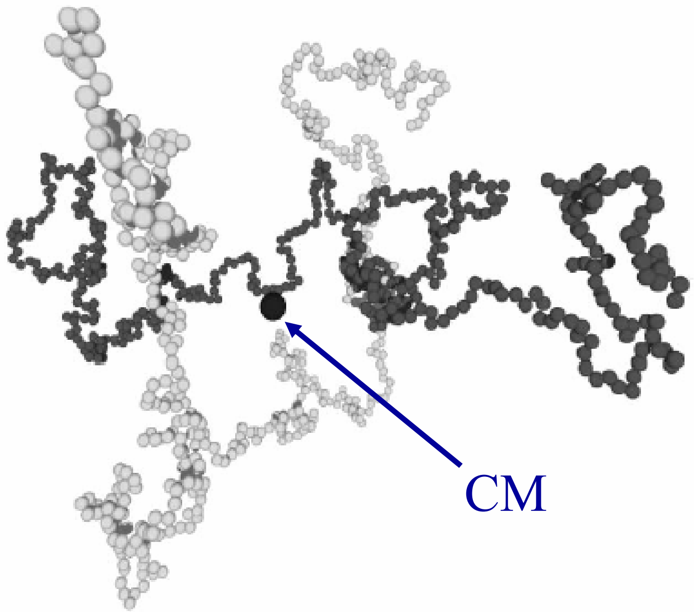
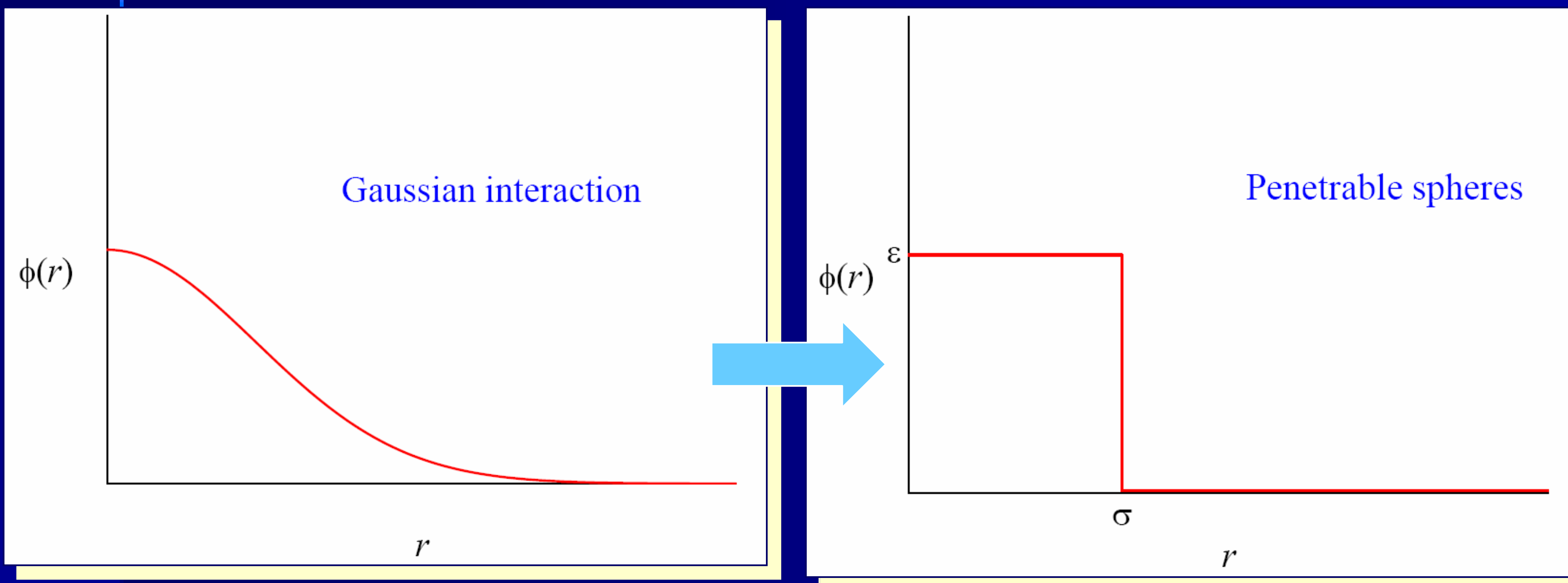


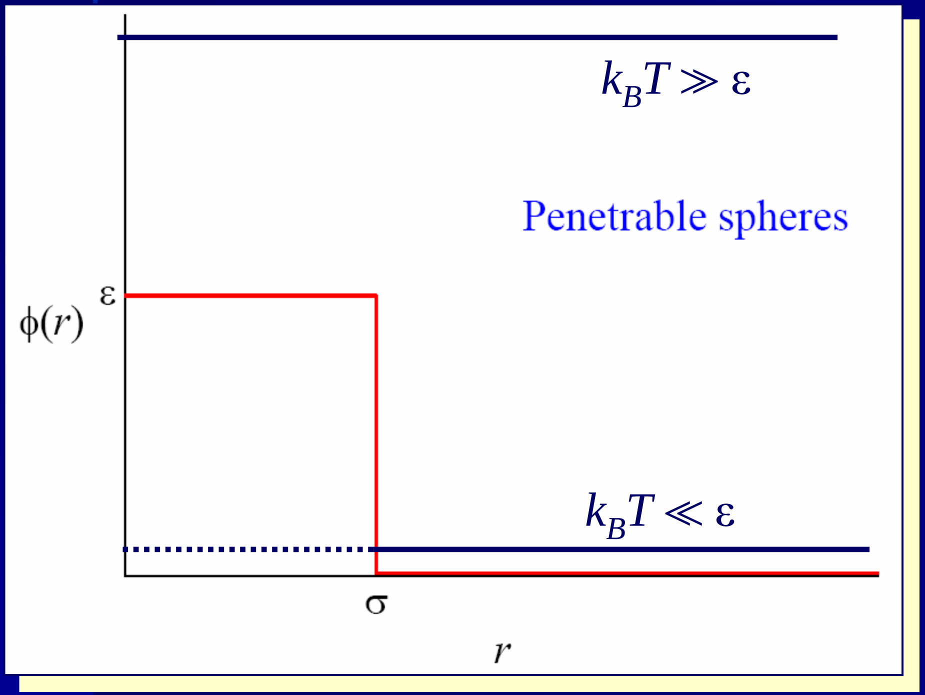
Fig. 14. A snapshot from a simulation involving two self-avoiding polymers. In this configuration, the centers of mass of the two chains (denoted by the big sphere) coincide, without violation of the excluded-volume conditions. (Courtesy of Arben Jusufi.)

C.N. Likos / Physics Reports 348 (2001) 267–439

Effective interaction between two polymer chains in a good solvent:



Aim: To propose and test two *analytical* approximations (one being exact in the high-temperature limit, the other one being exact in the low-temperature limit) for the structural properties of a 1D fluid



$T^* \equiv k_BT/\varepsilon$

$T^* \gg 1$: high-temperature (HT) approximation

$T^* \ll 1$: low-temperature (LT) approximation

Exact result in the high-temperature, high-density limit

[L. Acedo & A.S., PLA **323**, 427 (2004)]

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

$$x \equiv 1 - e^{-1/T^*}, \qquad T^* \to \infty \Rightarrow x \approx T^{*-1} \to 0$$

$$\boxed{\lim_{\substack{x\to 0\\ \rho\to\infty\\ \rho x = \text{finite}}} \quad y(r) = 1 + x w(r), \qquad w(r) = \frac{4\rho x}{\pi}\int_0^\infty dk \frac{\sin^2 k \cos kr}{k^2 + 2\rho x k \sin k}}$$

High-temperature (HT) *approximation*

$$y(r) = \frac{1}{1 - x w(r)}$$

Exact result in the zero-temperature limit (hard rods)

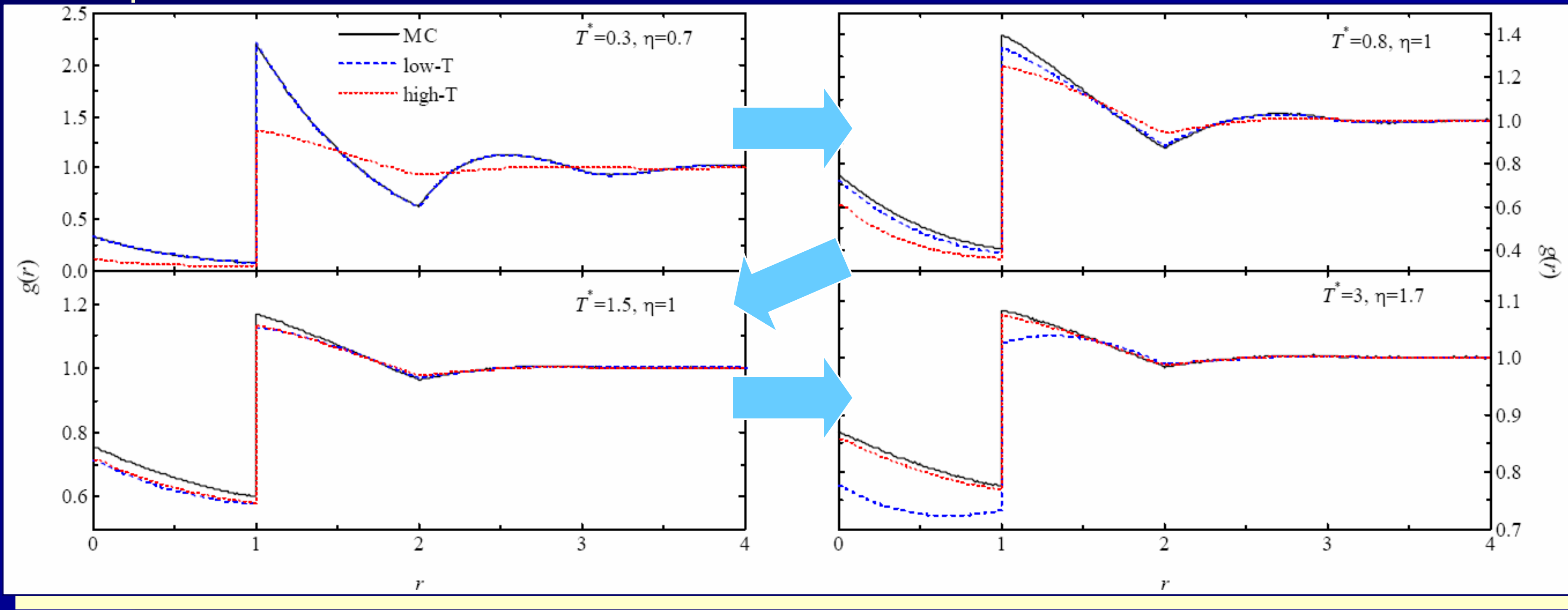
$G(t) \equiv \int_0^\infty dr\, g(r) e^{-rt}$: Laplace transform

$$\boxed{\rho \lim_{T^*\to 0} G(t) = \frac{P(t)}{1-P(t)}, \quad P(t) = \frac{\xi_0 e^{-t}}{t+\xi_0}, \quad \xi_0 \equiv \frac{\rho}{1-\rho}}$$

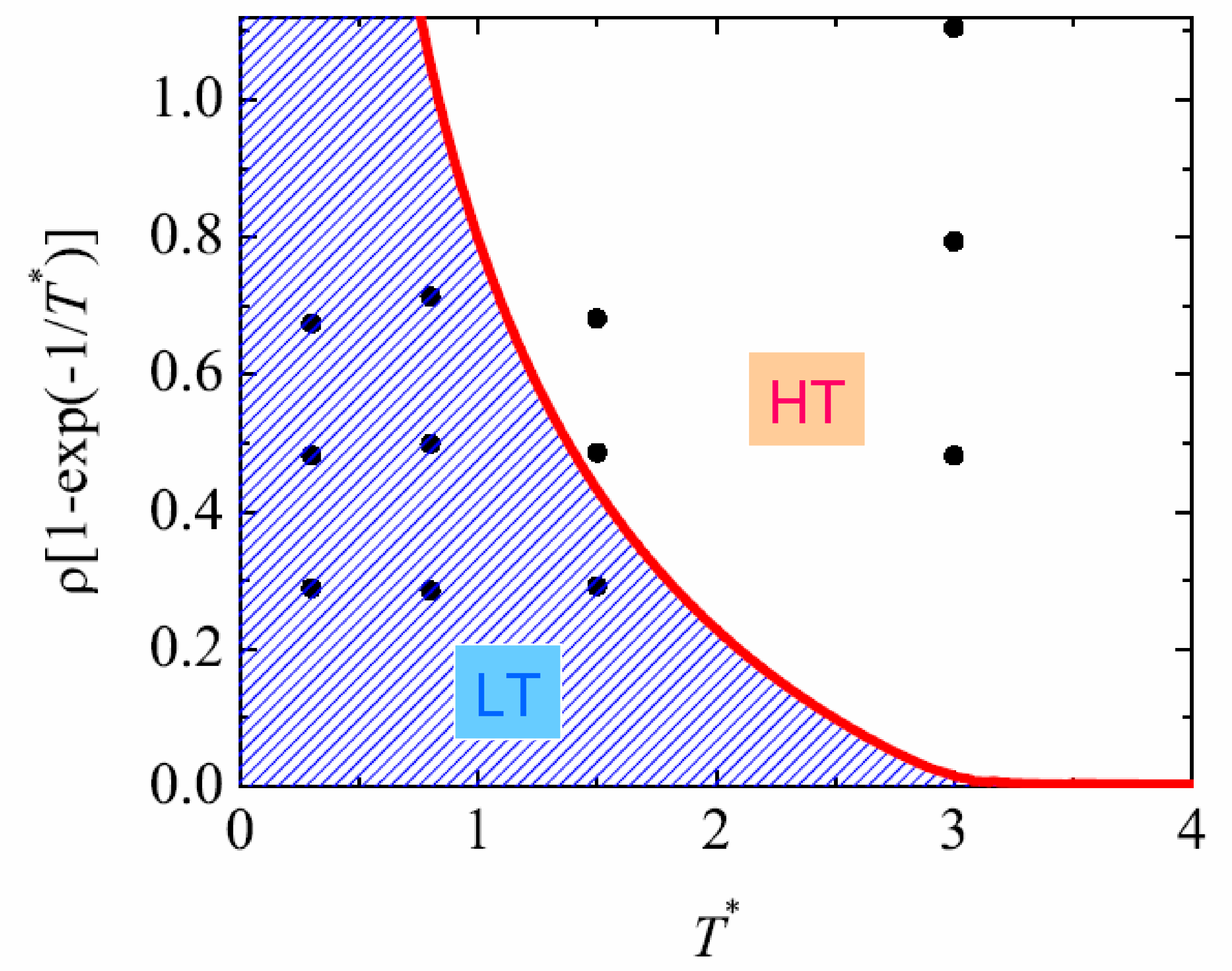
Low-temperature (LT) *approximation*

$$\rho G(t) = A\frac{1-t-e^{-t}}{t^2} + \frac{P(t)}{1-P(t)}, \quad P(t) = \frac{\xi - \xi' + \xi' e^{-t}}{t+\xi}$$

Comparison between MC simulations and the HT and LT approximations



“Basins” of the HT and LT approximations



Further work: the 3D case

- HT approximation:

$$y(r) = \frac{1}{1 - xw(r)}, \qquad w(r) = 96\pi\eta x \mathcal{F}^{-1}\left\{ \frac{(k\cos k - \sin k)^2}{k^3\left[k^3 - 24\eta x\,(k\cos k - \sin k)\right]} \right\}$$

- LT approximation:

$$g(r) = (r-1)\left[A + Br(r+1)\right]\Theta(1-r) + \frac{1}{12\eta r}\mathcal{L}^{-1}\left[t\frac{P(t)}{1+P(t)}\right]$$

$$P(t) = \frac{L_0 - 1 - e^{-t}(1 + L_1 t)}{1 + S_1 t + S_2 t^2 + S_3 t^3}$$