Beyond the single-file fluid using transfer-matrix method: Exact results for confined hard squares

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Abstract

We extend the transfer-matrix method for a system of **classical hard particles** with continuous translational degrees of freedom which are confined **in a narrow pore** but not form a single-file fluid, i.e. the pore is wide enough that the *particles can pass each other*. The particles in our two-dimensional system are hard squares confined between two parallel lines, where the pore width is between 2σ and 3σ (σ is the length of the square's side). Both the nearest neighbour and the next-nearest neighbour interactions are present in our formalism. The exact equation of state and the nearest neighbour distribution functions show that the effect of second neighbour interactions becomes relevant with increasing pore width and density. At intermediate densities the system forms a fluid phase with strong adsorption at the walls, while single square lattice structure develops continuously with increasing density at the vicinity of close packing.

Model

- hard squares in 2D confined between hard walls
- particels have continuous translational (but no rotational) degrees of freedom
- particels can pass each other: $\sigma < W < 2\sigma$

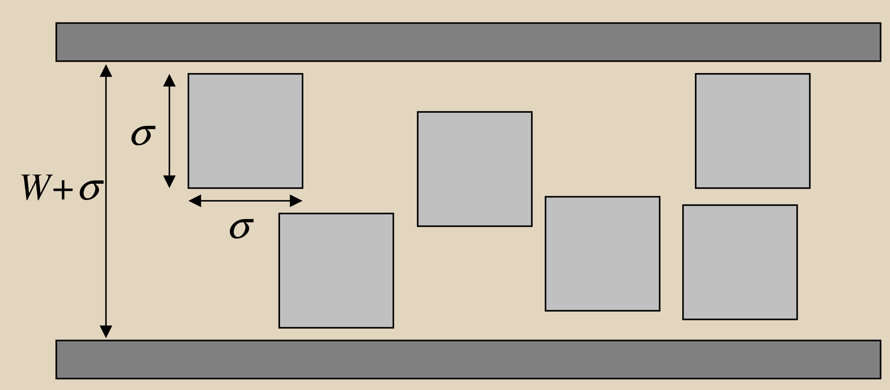

Figure 1: hard squares in a narrow channel

Conclusion

- The transfer matrix method can be extended for channels wide enough to exceed the single file fluid condition.
- In the case of narrower pore three different structures are observed:
  1. fluid with only one layer
  2. fluid with two layers
  3. solid-like structure with strongly correlating fluid layers

References

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M. J. Godfrey and M. A. Moore, *Phys. Rev. E.* **91**, 022120 (2015)

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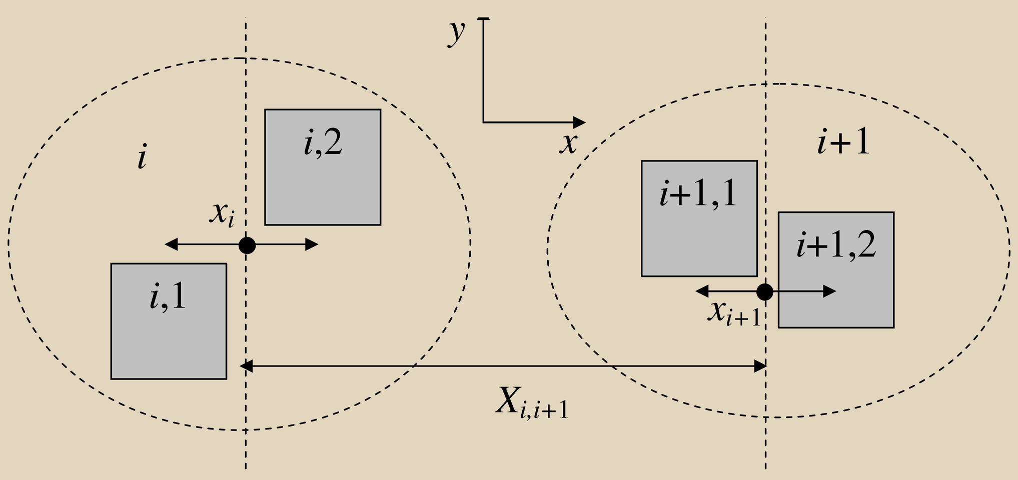
Transfer Matrix Methods

Particles with continuous degrees of freedom (position), partition function:

$$Z = \frac{1}{\Lambda^{2N}} \left(\prod_{i=1}^{N/2} \int_{-W/2}^{W/2} dy_{i,1}\, dy_{i,2} \int_{\sigma(y_{i,1},y_{i,2})}^{\infty} dx_i \right) \left(\prod_{j=1}^{N/2} \int_{\bar{\sigma}(y_{i,1},y_{i,2},x_i;y_{i+1,1},y_{i+1,2},x_{i+1})}^{\infty} dX_{i,i+1}\; e^{-\beta p_x W X_{i,i+1}} \right) = \frac{1}{\Lambda^{2N}} \mathrm{Tr}\, K^{N/2}$$



$$K = \frac{e^{-\beta p_x W \bar{\sigma}}}{\beta p_x W}$$

$\bar{\sigma}$ is the contact distance of the pairs

$$\mathrm{Tr}\, K^{N/2} = \lambda_0^{N/2}$$

Instead of compute the $2N$-fold integral in the partition function, we have to find the dominant eigenvalue, λ_0, of the followin eigenvalue equation:

$$\int_{-W/2}^{W/2} dy_{2,1}\, dy_{2,2} \int_{\sigma(y_{2,1},y_{2,2})}^{\infty} dx_2 \quad K(y_{1,1}, y_{1,1}, x_1; y_{2,1}, y_{2,1}, x_2)\, \psi(y_{2,1}, y_{2,1}, x_2) = \lambda\, \psi(y_{1,1}, y_{1,1}, x_1)$$

It can be done partly analytically, partly numerically.

Results

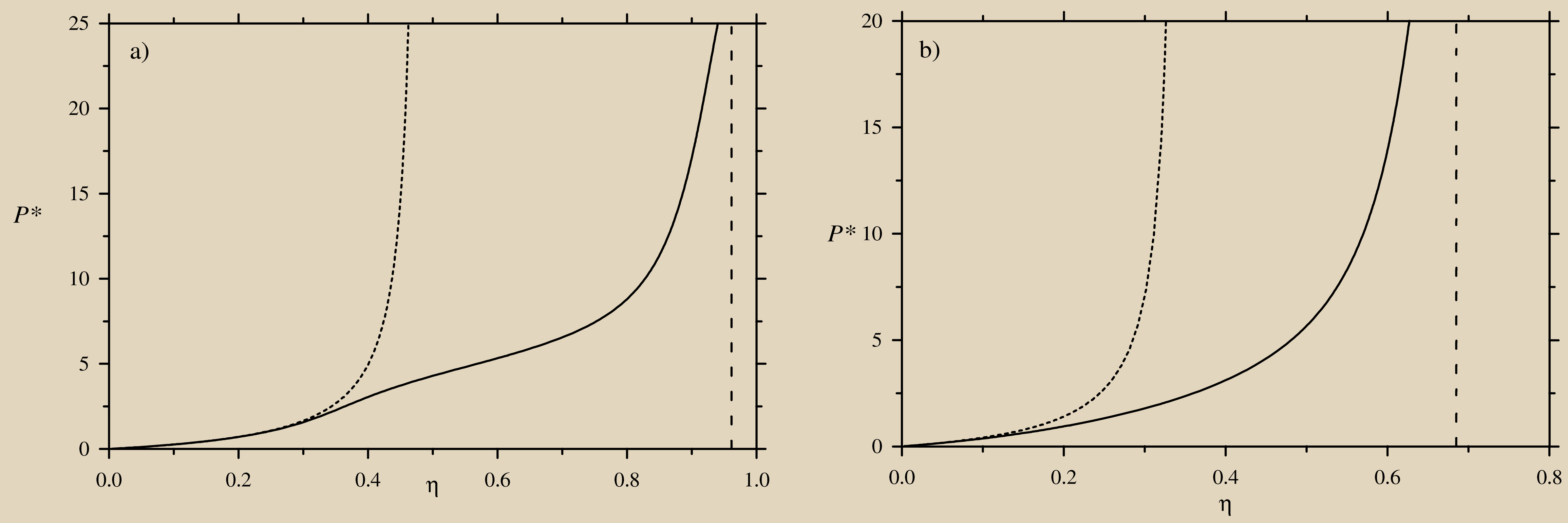


Figure 2: Equation of state for $W = 1.08\sigma$ (left), and $W = 1.92\sigma$ (right); $P^* = \beta P \sigma$ is the reduced pressure and $\eta = N\sigma^2/A$ is the packing fraction.

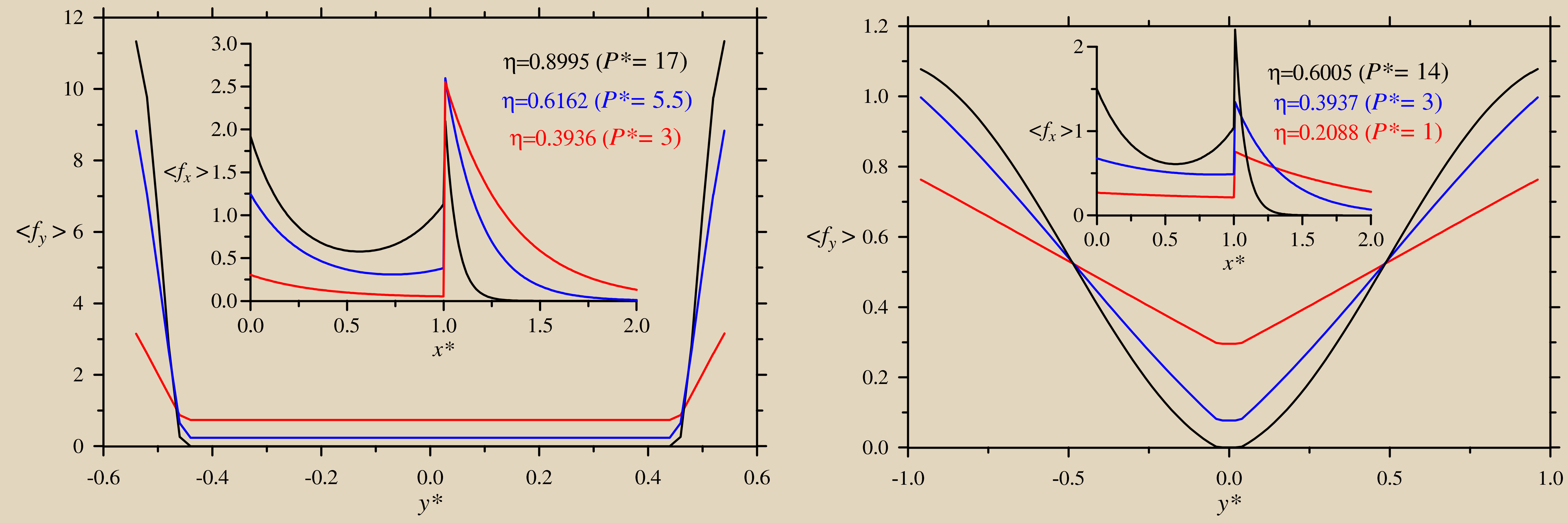


Figure 3: Transversal and longitudinal (insets) positional distribution functions of the hard squares for $W = 1.08\sigma$ (left), and $W = 1.92\sigma$ (right); $x^* = x/\sigma$ and $y^* = y/\sigma$

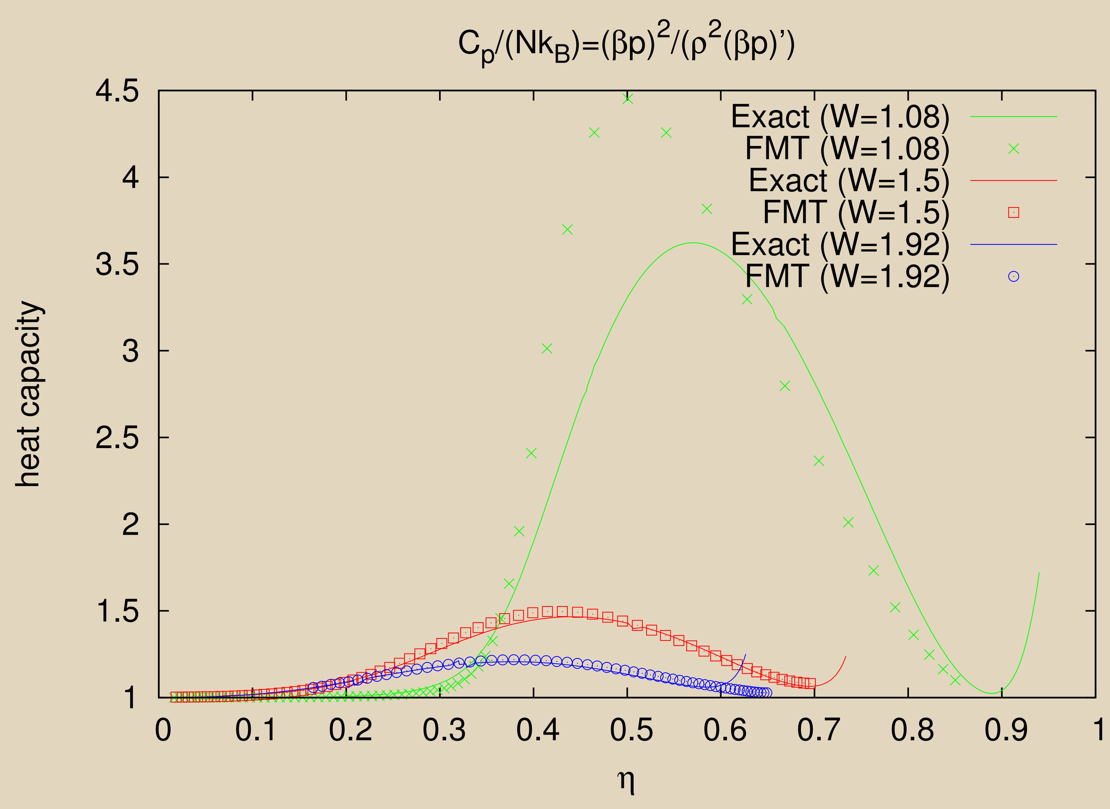


Figure 4: specific heat at constant pressure (c_p)