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 interactions are present in our formalism. The exact equation of state and the nearest neighbour interactions are present in our formalism.

Transfer Matrix Methods
Particles with continuous degrees of freedom (position), partition function:
\[
Z = \frac{1}{\Lambda^{2N}} \left( \prod_{i=1}^{N/2} d_{y_i} e^{-\beta p_{W} x_{i}} \right) \left( \prod_{i=1}^{N/2} d_{X_{i+1}} e^{-\beta p_{W} x_{i+1}} \right) = \frac{1}{\Lambda^{2N}} \text{Tr} K^{N/2}
\]

\[
K = e^{-\beta p_{W} \sigma} \frac{1}{\beta p_{W}}
\]

σ is the contact distance of the pairs

\[
\text{Tr} K^{N/2} = \lambda_{0}^{N/2}
\]

Instead of compute the 2N-fold integral in the partition function, we have to find the dominant eigenvalue, λ0, of the following eigenvalue equation:
\[
\int_{-W/2}^{W/2} \int_{-W/2}^{W/2} d_{y_{12}} d_{x_{12}} K(y_{1}, y_{1}, x_{1}; y_{2}, y_{2}, x_{2}) \psi(y_{1}, y_{2}, x_{1}, x_{2}) = \lambda \psi(y_{1}, y_{1}, x_{1})
\]

It can be done partly analytically, partly numerically.

Results

Figure 1: hard squares in a narrow channel

Figure 2: Equation of state for W = 1.08σ (left), and W = 1.92σ (right); P' = βPσ is the reduced pressure and η = Nσ^2/A is the packing fraction.

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

Figure 4: specific heat at constant pressure (c_p)

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

Acknowledgements
We acknowledge the financial support of the Hungarian State and the European Union under the TÁMOP-4.2.2.A-11/1/KONV-2013-0071.