Equation of state of hard-disk fluids under single-file confinement

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We consider a fluid of hard disks of unit diameter confined between two parallel walls separated by a distance $w = 1 + \epsilon$, so that each disk can only interact with its two nearest neighbors (single-file configuration, see Figure 1). The equation of state for this system was originally obtained by Kofke and Post [1] following the transfer-matrix method. It reads

$$Z = 1 + p\,\frac{\int_{-\epsilon/2}^{\epsilon/2} dy_1 \int_{-\epsilon/2}^{\epsilon/2} dy_2\, e^{-a(y_1-y_2)p} a(y_1-y_2)\phi(y_1)\phi(y_2)}{\int_{-\epsilon/2}^{\epsilon/2} dy_1 \int_{-\epsilon/2}^{\epsilon/2} dy_2\, e^{-a(y_1-y_2)p} \phi(y_1)\phi(y_2)},$$

where p is the longitudinal pressure (in units of k_BT), $Z = p/\lambda$ is the associated compressibility factor (λ being the longitudinal number density), $a(s) = \sqrt{1-s^2}$ is the longitudinal separation between two hard disks at contact with a transverse separation s, and $\phi(y)$ is the solution to the eigenfunction problem

$$\int_{-\epsilon/2}^{\epsilon/2} dy'\, e^{-a(y-y')p} \phi(y') = \ell\phi(y),$$

ℓ being the associated (maximum) eigenvalue. In this framework, $|\,\phi(y)|^2$ represents the probability density in the transverse direction.

In this work, we present two alternative approximations to this exact solution, a *basic* and an *advanced* one, that avoid having to numerically solve the integral eigenfunction equation and yield more manageable tools to characterize the equation of state of the system. In the *basic* approximation, based on the low-pressure limit behavior where particle density does not change along the transverse direction, $\phi(y)$ is assumed to be constant. This approximation not only yields the exact second virial coefficient, but it also reproduces the asymptotic behavior in the close-packing limit, although it overestimates the amplitude. The *advanced* approximation is based on the high-pressure behavior of the system, where particles accumulate more and more near the walls in two symmetric layers. More specifically, we assume $\phi(y) \propto e^{-a(y-\epsilon/2)p} + e^{-a(y+\epsilon/2)p}$. Consequently, this advanced approximation correctly reproduces the behavior in the high-pressure limit and, since it reduces back to the basic one for low pressures, it also produces the exact second virial coefficient.

Comparisons between these two approximations to results coming from both the exact equation and Monte Carlo simulations [1,2] show a good agreement of the *basic* approximation under low-pressure and/or narrow-pore conditions and a very good agreement of the *advanced* approximation for all ranges of pressure and pore sizes (see Figure 2).

REFERENCES

[1] D. A. Kofke and A. J. Post, J. Chem. Phys. **98** (1993), 4853-4861.
[2] K. K. Mon, Physica A **556** (2020), 124833.

FIGURES

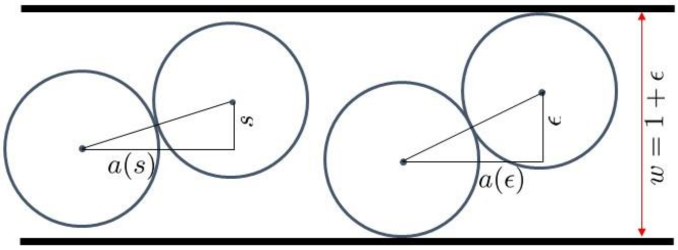

Figure 1: Schematic representation of the single-file hard-disk fluid.

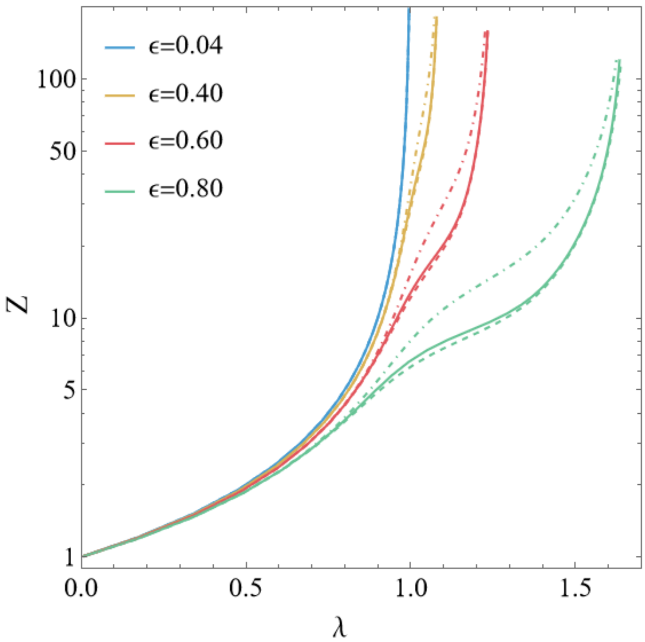

Figure 2: Equation of state for different values of the excess pore width ϵ for the exact solution (solid lines), the basic approximation (dash-dotted lines) and the advanced approximation (dashed lines).