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Radial distribution function of the hard sphere fluid

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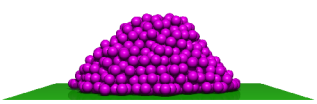

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Summary

We provide a formula (computer program) for the radial distribution function of the hard sphere fluid in the full range of reduced densities $\rho \in (0, 1.02]$ and separations $r \geq 1$.

The precision is better than 0.002 in the stable range $\rho \in (0, 0.943]$ and better than 0.004 for deeply metastable fluid.

Such a formula, including metastable states, is needed in perturbation theories of fluids.

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Definitions

- Diameter of hard spheres: σ=1
- (Reduced) number density: $\rho = \frac{N}{V}$
- Packing fraction: $y = \frac{\pi}{6}\rho$
- Radial distribution function (RDF):

$$g(r) = \left(1 - \frac{1}{N}\right) \frac{V}{4\pi r^2} \langle \delta(r - |\mathbf{r}_1 - \mathbf{r}_2|) \rangle_{\mathrm{NVT}}$$

  where $\langle\cdot\rangle_{\mathrm{NVT}}$ denotes NVT ensemble average and δ is the Dirac delta-function
- Total correlation function: $h(r) = g(r) - 1$

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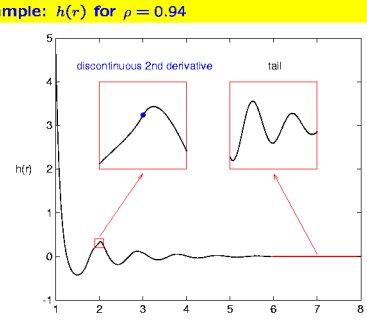
Example: $h(r)$ for $\rho = 0.94$



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Sources of data

- Molecular dynamics results[1], periodic boundary conditions, range of densities $\rho \in [0.2, 1.02]$ (incl. metastable states), NVT ensemble ($N = 13500$) corrected for finite size errors by:

$$g(r) \approx g_{\mu\mathrm{VT}}(r) = g_{\mathrm{NVT}}(r) + \frac{kT}{2N}\left(\frac{\partial\rho}{\partial p}\right)_T \frac{\partial^2\rho^2 g(r)}{\partial\rho^2} + \mathcal{O}(N^{-2})$$

  - $\left(\frac{\partial g}{\partial p}\right)_T$ from the Kolafa EOS[2]
  - $\frac{\partial^2\rho^2 g(r)}{\partial\rho^2}$ from OZ and Malijevský-Labík bridge function[3]
- Low-density expansion

$$h(r) = H_1(r)\rho + H_2(r)\rho^2 + \cdots \qquad (1)$$

  where H_1 and H_2 are known analytically (see Appendix)
- In future also: Equation of state ⇒ $g(1)$ (more accurate at contact)

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Strategy

- $r \in [1, 6]$: cubic splines, 80 equidistant subintervals of $d = 1/16$:

$$h(1 + id + \Delta r) = A_i + B_i\Delta r + C_i\Delta r^2 + D_i\Delta r^3, \quad \Delta r \in [0, d]$$

  Note that $r = 2$ is one of the partition points, in agreement with discontinuous $\mathrm{d}^2h/\mathrm{d}r^2$
  Spline coefficients A_i, B_i are fitted to polynomials in ρ:

$$A_i(\rho) = \rho^{\mathrm{floor}[r]} \sum_{j=0}^{8} A_{i,j}\rho^j \qquad (2)$$

  where floor[r] denotes rounding down to the nearest integer.
  Term $\rho^{\mathrm{floor}[r]}$ ensures consistency with the low-density expansion.
- $r > 6$:

$$h(r) = \frac{E_0}{\exp[E_1(r-1)]} \times \frac{\cos[E_2 + E_3(r-1)]}{r}$$

- $h(r)$ and its 1st derivative are continuous at all partition points $r = 1 + di$, $i \in [0, 80]$.

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Fitting procedure

- Fitting the tail (accuracy better than $5 \cdot 10^{-4}$ but $\rho = 1.02$):

$$\begin{aligned} E_0 &= 0.18 + \rho \\ E_1 &= 0.5125 - 1.7\ln(\rho) \\ E_2 &= 1.56\rho - 2.1 \\ E_3 &= 4.734 + 2.328\rho \end{aligned}$$

- Fitting the spline coefficients:
  A_i, B_i determined by the least-square method for every ρ, including $\rho = 0.001$ and $\rho = 0.002$ calculated from (1)
- Fitting A_i, B_i to polynomials in density
- Determining C_i, D_i from continuity conditions

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Results and discussion

The figure shows errors of the formulas for the range of densities. These errors are less than 0.002 for stable fluid (reduced density less than 0.95) and grow to 0.004 when metastable points are included.

Largest errors are close to contact and also in interval $r \in [5, 6]$ where the errors in the tail propagate (via the continuity conditions) to the splines.

The formulas can be improved in a number of ways, e.g.:

- fitting $\ln g(r)$ to suppress the increase of $h(r)$ near contact
- nonequidistant splines
- using $x = y/(1-y)$ instead of y or ρ
- more accurate tail expression and density dependence of E_i
- correct low-density tail
  term at $\ln\rho$ in E_1 should be 1, to be consistent with (1)
- including more terms in the low-density expansion (1)

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Appendix: Low-density expansion

$$H_1(r) = \circ\!-\!\circ$$

$$H_2(r) = \bowtie + \boxtimes + \sqsubset\!\sqsupset + \diagup\!\diagdown + \sqsupset\!\!-\!\!\sqsubset$$

where

$$\circ\!-\!\circ = \begin{cases} \frac{\pi}{12}(r+4)(r-2)^2 & \text{for } 1 \le r \le 2 \\ 0 & \text{for } r \ge 2 \end{cases}$$

$$\boxtimes = \left(\circ\!-\!\circ\right)^2$$

$$\sqsubset\!\sqsupset = \begin{cases} \frac{\pi^2}{1260r}(6 - 27r - 12r^2 - r^3)(r-3)^4 & \text{for } 1 \le r \le 3 \\ 0 & \text{for } r \ge 3 \end{cases}$$

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$$\diagup\!\diagdown = \boxtimes = \begin{cases} \frac{\pi^2}{1260r}(r^5 + 4r^4 - 51r^3 - 10r^2 + 479r - 81)(r-2)^2 & \text{for } 1 \le r \le 2 \\ 0 & \text{for } r \ge 2 \end{cases}$$

$$\sqsupset\!\!-\!\!\sqsubset = \begin{cases} -\frac{1}{2}\gamma_1^2(r) + X(r) & \text{for } 1 \le r \le \sqrt{3} \\ -\frac{1}{2}\gamma_1^2(r) & \text{for } \sqrt{3} \le r \le 2 \\ 0 & \text{for } r > 2 \end{cases}$$

$$\begin{aligned} X(r) = \frac{\pi}{2}\Bigg[& \left(-\frac{3}{280}r^4 + \frac{41}{420}r^2\right)\sqrt{3 - r^2} \\ & + \left(-\frac{23}{15}r + \frac{36}{35r}\right)\arccos\left(\frac{r}{\sqrt{12 - 3r^2}}\right) \\ & + \left(\frac{3}{560}r^6 - \frac{r^4}{15} + \frac{r^2}{2} + \frac{2r}{15} - \frac{9}{35r}\right)\arccos\left(\frac{r^2 + r - 3}{\sqrt{12 - 3r^2}}\right) \\ & + \left(\frac{3}{560}r^6 - \frac{r^4}{15} + \frac{r^2}{2} - \frac{2r}{15} + \frac{9}{35r}\right)\arccos\left(\frac{-r^2 + r + 3}{\sqrt{12 - 3r^2}}\right)\Bigg] \end{aligned}$$

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References

1. J. Kolafa, S. Labík, S., A. Malijevský, *Phys. Chem. Chem. Phys.* **6**, 2335 (2004).
2. A. Mulero, C. Galán, F. Cuadros, *Phys. Chem. Chem. Phys* **3**, 4991 (2001).
3. A. Malijevský, S. Labík, 1987, *Molec. Phys.* **60**, 663 (1987).
4. Computer program for $h(r)$ and data files with MD results are available at http://www.vscht.cz/fch/software/hsmd/

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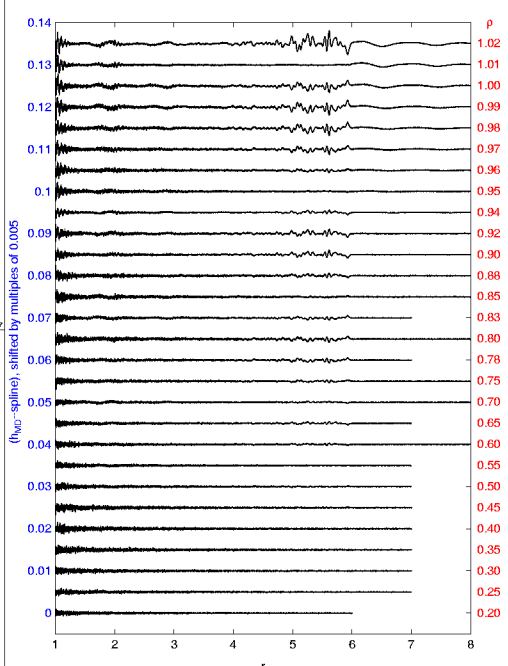
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