

# Specialization project

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# 1 Theory

## 1.1 Theoretical description of hard-sphere fluids

Hard-sphere (HS) fluids are fluids consisting of spherical particles interacting via the non-continuous potential

$$u = \begin{cases} \infty, & r < \sigma \\ 0, & r > \sigma. \end{cases} \quad (1)$$

$u$  is the interaction potential between two particles,  $r$  is the distance between them, and  $\sigma$  is the diameter of the particles. This potential makes it possible to analytically describe certain fluid properties using statistical mechanics. The HS potential is especially useful when modeling transport properties such as viscosity.

## 1.2 Transport properties

## 1.3 The viscosity of hard-sphere fluids

The central equation modeling the viscosity of HS fluids is the Enskog equation. This equation applies to one-component HS fluids consisting only of particles with the same mass  $m$  and radius  $\sigma$ . The viscosity of such fluids is (Di Pippo et al. 1977)

$$\eta(n, T) = \eta_0 \left[ g^{-1}(\sigma) + 0.8 V_{\text{excl}} \rho + 0.776 V_{\text{excl}}^2 \rho^2 g(\sigma) \right]. \quad (2)$$

Here,  $\eta^0 = \eta(0, T)$  is the viscosity of the fluid in the zero-density limit, and  $\chi$  is a radial distribution function at contact, describing the statistical distribution of particles around a pair of colliding particles. This determines how the collision frequency depends on the density of the fluid.  $\chi$  can be found for example using the system's equation of state, as done in (ibid.), a method referred to as Modified Enskog Theory.

In Enskog theory, a central assumption is that there is no correlation between different collisions. This means that the mean free time between collisions is much larger than the collision duration. The lack of correlated interactions does not work for real fluids with long range continuous interaction potentials. However, the assumption is more acceptable for low density HS-fluids. Enskog theory breaks down at high fluid densities, when collisions are too frequent to be uncorrelated, even for HS fluids.

## 1.4 Viscosity of mixtures

The Enskog equation was generalized by Thorne to describe two-component fluid mixtures (Chapman et al. 1953). A further generalization to mixtures of arbitrary component numbers has been performed by Tham and Gubbins (Tham et al. 1971). The results are outlined below, as presented in (Di Pippo et al. 1977).

The viscosity of a dense binary mixture of hard-sphere fluids is given by

$$\eta_{\text{mix}} = \left( \frac{y_1^2}{H_{11}} + \frac{y_2^2}{H_{22}} - \frac{2y_1y_2H_{12}}{H_{11}H_{22}} \right) \left( 1 - \frac{H_{12}^2}{H_{11}H_{22}} \right)^{-1} + \frac{3}{5}\bar{\omega}_{\text{mix}}, \quad (3)$$

where

$$y_1 = x_1 \left( 1 + \frac{1}{2}x_1\alpha_{11}\chi_{11}n + \frac{m_2}{m_1 + m_2}x_2\alpha_{12}\chi_{12}n \right), \quad (4)$$

and

$$\begin{aligned} H_{12} = H_{21} &= -\frac{2x_1x_2\chi_{12}}{\eta_{12}^0} \cdot \frac{m_1m_2}{(m_1 + m_2)^2} \left( \frac{5}{3A_{12}^*} - 1 \right), \\ H_{11} &= -\frac{x_1^2\chi_{11}}{\eta_1^0} + \frac{2x_1x_2\chi_{12}}{\eta_{12}^0} \cdot \frac{m_1m_2}{(m_1 + m_2)^2} \left( \frac{5}{3A_{12}^*} + \frac{m_2}{m_1} \right), \end{aligned} \quad (5)$$

and where  $y_2$  and  $H_{22}$  follows from exchanging the subscripts in  $y_1$  and  $H_{11}$  respectively.  $A_{12}^*$  is a dimensionless ratio of collision integrals (of type  $ij$ ). For hard spheres,  $A_{12}^*$  is exactly unity, and for other forms of interaction, it is close to unity.  $\chi_{ij} = \chi_{ji}$  are radial distribution functions for molecules of type  $i$  colliding with molecules of type  $j$ , similar to the one-component function  $\chi$  above. Finally,  $\bar{\omega}_{\text{mix}}$  can be written

$$\begin{aligned} \bar{\omega}_{\text{mix}} &= x_1^2\bar{\omega}_{11} + x_1x_2\bar{\omega}_{12} + x_2^2\bar{\omega}_{22}, \text{ where} \\ \bar{\omega}_{ij} &= \frac{4}{9}n^2\sigma_{ij}^4\chi_{ij}\sqrt{\frac{2\pi m_1m_2kT}{m_1 + m_2}} \text{ for } i, j = 1, 2. \end{aligned} \quad (6)$$

## 1.5 Simulation of hard-sphere fluids

Several methods exist for simulating fluids consisting of rigid spheres. While Monte Carlo methods are relatively simple to use with hard-sphere potentials, molecular dynamics methods allow calculating dynamical and out-of-equilibrium properties of a system (Allen et al. 1989).

Jover et al. (Jover et al. 2012) has shown that a Mie (or generalized Lennard-Jones) potential

$$u_{\text{Mie}}(r) = \frac{\lambda_r}{\lambda_r - \lambda_a} \left( \frac{\lambda_r}{\lambda_a} \right)^{\frac{\lambda_a}{\lambda_r - \lambda_a}} \epsilon \left[ \left( \frac{\sigma}{r} \right)^{\lambda_r} - \left( \frac{\sigma}{r} \right)^{\lambda_a} \right], \quad (7)$$

can approximate a hard-sphere interaction potential.  $\epsilon$  is the depth of the potential at its minimal value, and  $\lambda_r$  and  $\lambda_a$  define the strength of the repulsive and attractive parts of the potential. As in 1,  $\sigma$  and  $r$  are the diameter and relative distance of the interacting particles.

The repulsive part of the Mie potential can be isolated by shifting it upwards by its minimal value  $\epsilon$  and cutting it off there. Thus, the potential is exactly zero once it has

reached its minimum. This gives a steep non-negative potential of the form

$$u_{(\lambda_a, \lambda_b)}(r) = \begin{cases} \frac{\lambda_r}{\lambda_r - \lambda_a} \left( \frac{\lambda_r}{\lambda_a} \right)^{\frac{\lambda_a}{\lambda_r - \lambda_a}} \epsilon \left[ \left( \frac{\sigma}{r} \right)^{\lambda_r} - \left( \frac{\sigma}{r} \right)^{\lambda_a} \right] + \epsilon, & r < \sigma \left( \frac{\lambda_r}{\lambda_a} \right)^{\frac{1}{\lambda_r - \lambda_a}} \\ 0, & r > \sigma \left( \frac{\lambda_r}{\lambda_a} \right)^{\frac{1}{\lambda_r - \lambda_a}}, \end{cases} \quad (8)$$

closely resembling that of an infinitely steep hard wall potential (equation 1). This potential is referred to as a pseudo hard-sphere potential. Jover et al. chose the exponents  $(\lambda_r, \lambda_a) = (50, 49)$ , as a compromise between faithfulness of the pseudo hard representation towards the perfectly hard wall, and computational speed. Higher exponents will produce a steeper repulsion. This however, comes at a cost. The steeper the potential, the shorter time steps are needed to ensure that the computations are precise. Therefore, steeper repulsions are computationally more expensive to simulate.

Writing it out for clarity, the Mie (50, 49) potential has the form

$$u_{(50, 49)}(r) = \begin{cases} 50 \left( \frac{50}{49} \right)^{49} \epsilon \left[ \left( \frac{\sigma}{r} \right)^{50} - \left( \frac{\sigma}{r} \right)^{49} \right] + \epsilon, & r < \frac{50}{49} \sigma \\ 0, & r > \frac{50}{49} \sigma. \end{cases} \quad (9)$$

Pousaneh and de Wijn (Pousaneh et al. 2020) have shown that such a pseudo-hard sphere potential can be used to model viscosity for a one-component hard-sphere fluid, and that the obtained viscosity is in agreement with Enskog theory.

## References

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