# Specialization project

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## Contents

# 1 Theory

## 1.1 Theoretical description of the viscosity of hard-sphere fluids

Enskog theory describes transport properties of hard sphere fluids, as an approximation to real gas behaviour. Of particular interest for this work is the Enskog equation for the viscosity of such fluids, consisting of *one* type of particle, of mass $m$ and diameter $\sigma$.

$$\begin{aligned} \eta(n,T) &= \frac{\eta^0}{\chi}(1+\frac{1}{2}\alpha\chi n)^2 + \frac{3}{5}\bar{\omega}, \quad \text{where} \\ \alpha &= \frac{8}{15}\pi\sigma^3, \quad \text{and} \\ \bar{\omega} &= \frac{4}{9}n^2\sigma^4\chi\sqrt{\pi m \mathrm{k}T}. \end{aligned} \tag{1}$$

Here, $\eta^0 = \eta(0,T)$ is the viscosity 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.

The Enskog equation was generalized by Thorne to describe two-component fluid mixtures(Chapman et al. 1953), and 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

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

where

$$y_1 = x_1\left(1 + \frac{1}{2}x_1\alpha_{11}\chi_{11}n + \frac{m_2}{m_1+m_2}x_2\alpha_{12}\chi_{12}n\right), \tag{3}$$

and

$$\begin{aligned} H_{12} = H_{21} &= -\frac{2x_1x_2\chi_{12}}{\eta_{12}^0}\cdot\frac{m_1m_2}{(m_1+m_2)^2}\left(\frac{5}{3A_{12}^*} - 1\right), \\ H_{11} &= -\frac{x_1^2\chi_{11}}{\eta_1^0} + \frac{2x_1x_2\chi_{12}}{\eta_{12}^0}\cdot\frac{m_1m_2}{(m_1+m_2)^2}\left(\frac{5}{3A_{12}^*} + \frac{m_2}{m_1}\right), \end{aligned} \tag{4}$$

and where $y_2$ and $H_{22}$ follows from exchanging the subscripts in $y_1$ and $H_{11}$ respectively. $\chi_{ij} = \chi_{ji}$ are radial distrubution functions for molecules of type $i$ colliding with molecules of type $j$.

## 1.2 Simulation of hard-sphere fluids

Several methods exist for simulating fluids consisting of hard spheres. While Monte Carlo methods are relatively simple to use with hard sphere potentials, that is, spherical particles (molecules) via non-continuous interaction potential of the form

$$u = \begin{cases} \infty, & r < \sigma \\ 0, & r > \sigma, \end{cases} \tag{5}$$

molecular dynamics methods allow calculating dynamical and out-of-equilibrium properties of a system (Allen et al. 1989).

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

$$u_{\mathrm{Mie}}(r) = \frac{\lambda_r}{\lambda_r - \lambda_a} \left(\frac{\lambda_r}{\lambda_a}\right)^{\frac{\lambda_a}{\lambda_r - \lambda_a}} \epsilon \left[ \left(\frac{\sigma}{r}\right)^{\lambda_r} - \left(\frac{\sigma}{r}\right)^{\lambda_a} \right], \tag{6}$$

can approximate a hard-sphere interaction potential well, when the repulsive part of the Mie potential is isolated, by shifting it upwards by its minimal value (the well depth $\epsilon$), and cutting it off here, setting the potential to zero once it has reached its minimum. This gives a steep non-negative potential of the form

$$u_{(\lambda_a,\lambda_b)}(r) = \begin{cases} \frac{\lambda_r}{\lambda_r - \lambda_a} \left(\frac{\lambda_r}{\lambda_a}\right)^{\frac{\lambda_a}{\lambda_r - \lambda_a}} \epsilon \left[ \left(\frac{\sigma}{r}\right)^{\lambda_r} - \left(\frac{\sigma}{r}\right)^{\lambda_a} \right] + \epsilon, & r < \sigma \left(\frac{\lambda_r}{\lambda_a}\right)^{\frac{1}{\lambda_r - \lambda_a}} \\ 0, & r > \sigma \left(\frac{\lambda_r}{\lambda_a}\right)^{\frac{1}{\lambda_r - \lambda_a}}, \end{cases} \tag{7}$$

closely resembling that of an infinitely steep hard wall potential. Jover et al. chose the exponents $(\lambda_r, \lambda_a) = (50, 49)$ as a compromise between the faithfulness of the pseudo hard representation and computational speed: Higher exponents will give steeper potentials, but at the expense of making simulations more time-consuming, because shorter time steps are needed. For clarity, the Mie (50, 49) potential has the form

$$u_{(50,49)}(r) = \begin{cases} 50 \left(\frac{50}{49}\right)^{49} \epsilon \left[ \left(\frac{\sigma}{r}\right)^{50} - \left(\frac{\sigma}{r}\right)^{49} \right] + \epsilon, & r < \frac{50}{49}\sigma \\ 0, & r > \frac{50}{49}\sigma. \end{cases} \tag{8}$$

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

# References


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