Specialization project

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Contents

1 Theory

1.1 Theoretical description of hard-sphere fluids

Hard-sphere fluids, meaning fluids constisting of spherical particles (molecules) interacting via the non-continuous potential

$$u = \begin{cases} \infty, & r < \sigma \\ 0, & r > \sigma, \end{cases} \tag{1}$$

can model real gas behaviour, and has been an important way to describe fluid and gas states in statistical mechanics. Enskog theory is one framework which describes transport properties of such fluids. In Enskog theory, a central assumption is that there is no correlation between different collisions, meaning that the mean free time between collisions is much larger than the collision duration. While this assumption gives useful results, it also means that Enskog theory breaks down at high fluid densities, when collisions are too frequent to be uncorrelated.

1.2 The viscosity of hard-sphere fluids

Of particular interest for this work is the Enskog equation for the viscosity of one-component hard-sphere fluids: Fluids consisting only of particles with the same mass m and radius σ, interacting via the potential described in equation 1. The viscosity of such fluids is (Di Pippo et al. 1977)

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

Here, $\eta^0 = \eta(0,T)$ is the viscosity of the fluid in the zero-density limit, and χ 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. χ can be found for example using the system's equation of state, as done in (ibid.), a method referred to as Modified Enskog Theory.

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

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

where

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

and

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

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 distrubution functions for molecules of type i colliding with molecules of type j, similar to the one-component function χ above. Finally, $\bar{\omega}_{\text{mix}}$ can be written

$$\begin{aligned} \bar{\omega}_{\text{mix}} &= x_1^2\bar{\omega}_{11} + x_1x_2\bar{\omega}_{12} + x_2^2\bar{\omega}_{22}, \text{where} \\ \bar{\omega}_{ij} &= \frac{4}{9}n^2\sigma_{ij}^4\chi_{ij}\sqrt{\frac{2\pi m_1m_2\text{k}T}{m_1+m_2}} \text{for} i,j = 1,2. \end{aligned} \tag{6}$$

1.3 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).

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

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

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 ϵ), and cutting it off there, setting the potential to zero once it has reached its minimum. This gives a steep non-negative potential of the form

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

closely resembling that of an infinitely steep hard wall potential (equation 1). 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 give steeper potentials, but at the expense of making simulations more time-consuming, because shorter time steps are needed.

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

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

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 hard-sphere fluid, and that the obtained viscosity is in agreement with Enskog theory. However, to the best of our knowledge, such a confirmation has not been published for fluids of more than one component.

References

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