Specialization project

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Contents

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

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

u is the interaction potential between two particles, r is the distance between them, and σ 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 σ. The viscosity of such fluids is (Di Pippo et al. 1977)

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

Here, $\eta^0 = \eta(0, T)$ is the viscosity of the fluid in the zero-density limit. V_{excl}, the excluded volume, is the part of the fluid which one cannot occupy, because it is occuied by other particles. V_{excl} is commonly assumed to be the volume of all particles in the fluid. This however, is only correct in the zero-density limit. When the fluid density is higher, the space in between particles may also be unavailable.

Lastly, in equation (2), $g(\sigma)$ is a radial distribution function at contact. $g(\sigma)$ is the probability distribution of particles around one particle in the fluid. This determines how the collision frequency depends on the density of the fluid. $g(\sigma)$ can be found for example using the system's equation of state, as done in (ibid.). This method is referred to as Modified Enskog Theory.

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

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

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, $\bar{\omega}_{\mathrm{mix}}$ can be written

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

1.5 Simulation of hard-sphere fluids

Several methods exist for simulating fluids consisting of rigid spheres. While Monte Carlo (MC) methods are relatively simple to use with hard-sphere potentials, molecular dynamics (MD) methods allow calculating dynamical and out-of-equilibrium properties of a system (Allen et al. 1989). This section gives an introduction to both Monte Carlo and molecular dynamics, focusing especially on molecular dynamics for hard and pseudo-hard spheres.

1.5.1 Monte Carlo methods

1.5.2 Event-driven MD simulation

A simple method for hard sphere simulations in molecular dynamics is an event-driven HS simulation. Key elements of this simultion is outlined below.

Compute the time until a collision occurs, for all particles in the system. All collisions are stored in a list containing at least information about the time of the collision, and the identity of the two involved particles. Then, the time until the earliest collision is identified by searching through the list. Using Newton's equations of motion, all atoms are propagated freely until the collision happens. Through conservation laws, the colliding particles' velocities are then updated. Their next collisions are then added to the list of upcoming collisions. This process is repeated, and all atom positions are updated with the time until the next collision in the list.

It should be noted that after a collision happens, other collisions involving either of the two particles will be invalid. These should be discarded from the list.

1.5.3 Continuous potential MD simulation methods

There are several powerful and efficient molecular dynamics programmes available, including LAMMPS, GROMACS, DL_POLY and NAND. These do, however, not handle discontinous potentials. Thus, the event-driven method is not supported by any of these programmes (Allen et al. 1989). In order to utilize the efficiency of the available MD software, it is more convenient to use a different method. The hard sphere potential can be approximated with a steep but continuous interaction potential instead. Then, the particle positions are updated using numerical integration methods with short, finite time steps.

Additionally, once there are long-range interaction forces between particles, the event driven simulation does not work, and integration methods are required. Therefore, continuous potential modelling is much more useful for realistic fluid models.

Several potentials are possible to use as hard-sphere approximations. The Lennard-Jones potential is a well-known example of historical importance. In order to model hard sphere potentials, it should be modified so that it's repulsive component is isolated. The resulting non-attractive potential is known as a WCA-potential.

Increased computer efficiency makes steeper potentials more appropriate. In particular, Jover et al. (Jover et al. 2012) has shown that a Mie (or generalized Lennard-Jones) potential

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

can approximate the hard-sphere interaction potential. ϵ is the depth of the potential at it's minimal value, and λ_r and λ_a define the strength of the repulsive and attractive parts of the potential. As in (1), σ 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 ϵ and cutting it off there. Thus, the potential is excactly 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)). 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 precice. Therefore, steeper repulsions are computationally more expensive to simulate.

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

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

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.

1.6 Measuring the viscosity of a fluid in NEMD

Müller-Plathe (Müller-Plathe 1999) has proposed a method of computing the viscosity of a fluid in nonequilibrium molecular dynamics (NEMD) simulations.

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