Project thesis

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Contents

1 Theory

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) wia non-continous interaction potential of the form

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

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

$$u_{\text{Mie}}(r) = \frac{\lambda_r}{\lambda_r - \lambda_a} \left(\frac{\lambda_r}{\lambda_a}\right)^{\frac{\lambda_a}{\lambda_r - \lambda_a}} \epsilon \left[\left(\frac{\sigma}{r}\right)^{\lambda_r} - \left(\frac{\sigma}{r}\right)^{\lambda_a}\right], \tag{2}$$

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 here, setting the potential to zero once it has reached its minimum. This gives a steep non-negative potential of the form

$$u_{(\lambda_a,\lambda_b)}(r) = \begin{cases} \frac{\lambda_r}{\lambda_r - \lambda_a} \left(\frac{\lambda_r}{\lambda_a}\right)^{\frac{\lambda_a}{\lambda_r - \lambda_a}} \epsilon \left[\left(\frac{\sigma}{r}\right)^{\lambda_r} - \left(\frac{\sigma}{r}\right)^{\lambda_a}\right] + \epsilon, & r < \sigma \left(\frac{\lambda_r}{\lambda_a}\right)^{\frac{1}{\lambda_r - \lambda_a}} \\ 0, & r > \sigma \left(\frac{\lambda_r}{\lambda_a}\right)^{\frac{1}{\lambda_r - \lambda_a}}, \end{cases} \tag{3}$$

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 faithfullness of the pseudo hard representation and comptational 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

$$u_{(50,49)}(r) = \begin{cases} 50\left(\frac{50}{49}\right)^{49}\epsilon\left[\left(\frac{\sigma}{r}\right)^{50} - \left(\frac{\sigma}{r}\right)^{49}\right] + \epsilon, & r < \frac{50}{49}\sigma \\ 0, & r > \frac{50}{49}\sigma. \end{cases} \tag{4}$$

References

Allen, M.P., D. Frenkel, and J. Talbot (1989). "Molecular dynamics simulation using hard particles". In: *Computer Physics Reports* 9.6, pp. 301–353. ISSN: 0167-7977. DOI: https://doi.org/10.1016/0167-7977(89)90009-9. URL: https://www.sciencedirect.com/science/article/pii/0167797789900099.

Jover, J. et al. (2012). "Pseudo hard-sphere potential for use in continuous molecular-dynamics simulation of spherical and chain molecules". In: *The Journal of Chemical Physics* 137.14, p. 144505. DOI: 10.1063/1.4754275. eprint: https://doi.org/10.1063/1.4754275jkjk. URL: https://doi.org/10.1063/1.4754275.