

Studies of Shear Viscosity of Hard Chain Fluids

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Abstract

This research focused on the viscosity of hard chain fluids. This study was initiated with an investigation of the equilibrium molecular dynamics simulations of pure hard-sphere molecules. The natural extension of that work was to hard chain fluids. This is because the algorithms for hard sphere fluids and hard chain fluids can be developed in the same manner. The hard chain model is one in which each molecule is represented as a chain of freely jointed hard spheres that interact on a site-site basis. The major use of the results from this study lie in the development of a transport perturbation theory in which the hard chain serves as the reference. Simulations were performed on different systems: hard spheres, 2-mers, 4-mers and 8-mers. The systems reduced temperature was fixed at unity and the density was varied over the range of fluid states. The calculation of static properties and shear viscosity are based on an atomic reference. The major use of the results from this study lie in the future development of a transport perturbation theory in which the hard chain serves as the reference. Comparisons are made to the previous studies of Alder and Wainwright¹ and Smith *et al.*². Our results show agreement to within the combined uncertainties with both of these studies. Comparisons have also been made to a modified Enskog theory. Results show the failure of the Enskog theory to predict the high density viscosity and that the theory fails more rapidly with density as the chain length increases. We attribute this to a failure of the molecular chaos assumption used in the Enskog theory. Further comparisons are made to real fluids using the SAFT-MET and TRAPP approaches. As expected, the hard sphere model is not appropriate to estimate properties of real fluids. However, the hard sphere model provide the good starting to be serve as the reference basis to study chain molecule systems.

Keywords : Molecular Dynamics, Hard Chain Fluids, Viscosity, Enskog theory, SAFT, TRAPP

Extended Abstract

Introduction and Theory

In the past, the principal use of computer simulation data was to provide “experimental” data for model systems that could be used to test theories developed with an analytical approach. Today, simulations are not only used to test theory, but also to make nearly quantitative estimates of thermophysical properties of real fluids. In addition, molecular simulation provides nano-scale information that can be used to design new materials and, in principle, processing strategies. In fact, the primary factor limiting the accuracy of molecular scale simulations is the accuracy of the force fields, which are used to model the interactions between the molecular species. With the recent rapid growth in computational power coupled with rapidly decreasing costs of hardware, microscopic computer simulation has become a very important tool in science and engineering today. The focus of this work is on the accuracy of the methods by which they can be simulated and on the development of a simple model for complex (chain) fluids, in particular, the simulation and modeling of viscosity hard chain fluids.

Real molecules are usually polyatomic except for the noble gases and metals, so it is important to study the structure and behavior of chain molecules. Although considerable progress has been achieved for monatomic fluids in the past few decades, it has been only in recent years that there has been much work on the chain fluids. The ultimate goal of this study was to develop a theoretically based viscosity model by modifying the Enskog theory and the Statistical Associating Fluid Theory (SAFT).

The only analytic theory for dense fluid transport prediction is known as the Enskog theory (and its modifications) which was developed for hard spheres. However, the hard sphere model retains much of the correct character of liquid behavior because molecules in liquids are packed so closely together, repulsive forces tend to dominate the structure and properties of dense fluids. Because of this, the hard sphere model is particularly popular for use as a reference in the development of perturbation theories. A good example of a perturbation theory for the equilibrium properties of chain fluids is the SAFT theory proposed by Chapman *et al.*^{3,4} and Huang and Radosz⁵. In the SAFT theory, a chain molecule is described as a “string” of linked hard sphere segments with an attractive square well interaction between the segments. In addition, this SAFT theory allows for hydrogen bonded interactions between segments on different molecules. Unfortunately, there is no analogous perturbation theory for the transport properties of chain fluids. In this portion of our study we have started an investigation of the viscosity of hard chain fluids by generating quasi-experimental data through the use of molecular dynamics. Our ultimate goal is develop a modified Enskog theory for hard chain fluids that could then be used to develop a perturbation theory for fluid transport properties.

Molecular dynamics experiments

The model for hard chain fluids used in this work was proposed by Rapaport^{6,7} such that chain molecules contain of a number of hard spheres connected each other by small links. There is no restriction on the movement of spheres except for the condition that they cannot overlap. The advantage of this model is that the original hard sphere MD approach proposed by Alder and Wainwright can be used: the coupled motion between the adjacent spheres can be treated as that of a collection of separated spheres. The hard chain molecule and their site-site interactions with different chain molecules are shown in Figure 1.

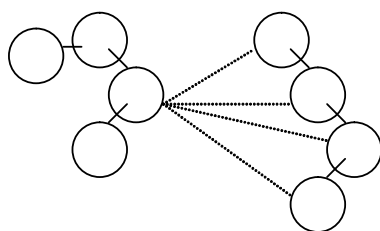


Figure 1 Hard chain model and their site-site interactions with different chain molecules.

The simulation study is focused on viscosity of short chain molecules and covers the region from low to high density, up to the fluid-solid transition. Although this study is focused on short chain fluids, the simulation approach provides the basis for long chain simulation studies in the future. In this study, Simulations were performed on four different systems: hard spheres (1-mers), 2-mers, 4-mers and 8-mers. The systems' reduced temperature was fixed at unity and the density was varied over the range of fluid states. The simulation time depends on the chain lengths because higher chain length fluids need longer times for relaxation. The basic methodology is as follows. After an initial configuration was provided to the system, a cell list is constructed and

a neighbor list is utilized to find the nearest neighbor within a preset radius. The collision time list is constructed only with these neighbors. If a neighboring particle is in the same chain and next to the central particle, a time list for a possible full extension collision must be evaluated. The “pair” with the minimum collision time is selected to be the next collision. After the collision, all particles are moved, the velocities of two colliding particles are reevaluated and the neighbor lists of the two colliding particles and their neighbors must be updated. The dynamic variables are collected every n steps. Then the calculation process is repeated.

Results

Figure 1 is the results of MD pseudo-experimental data which are compared to results from Alder and Wainwright¹ and Smith et al.². These simulation results are compared to both the original Enskog theory and its modification which takes into account a thermal pressure. The agreement between the MD and Enskog is poor at high densities for hard spheres and hard sphere chains. A close examination of these trends shows that failure happens at lower densities for higher chain lengths. These failures can be attributed to failures of the molecular chaos assumption in the high density region. Comparisons with the TRAPP model show that the trends of shear viscosity prediction by TRAPP increase with number segment increases. As expected, the agreement between the hard sphere simulation data and real fluid TRAPP prediction is rather poor, although the general trends with density are very similar. It is encouraging, however, that the hard sphere results systematically lie under the real fluid results—the indication being that it may be possible to use the modified Enskog representation of the simulation data as the reference contribution in perturbation theory. The inclusion of attractive forces will increase the calculated viscosity as shown in the results of MET-SAFT which includes dispersion forces.

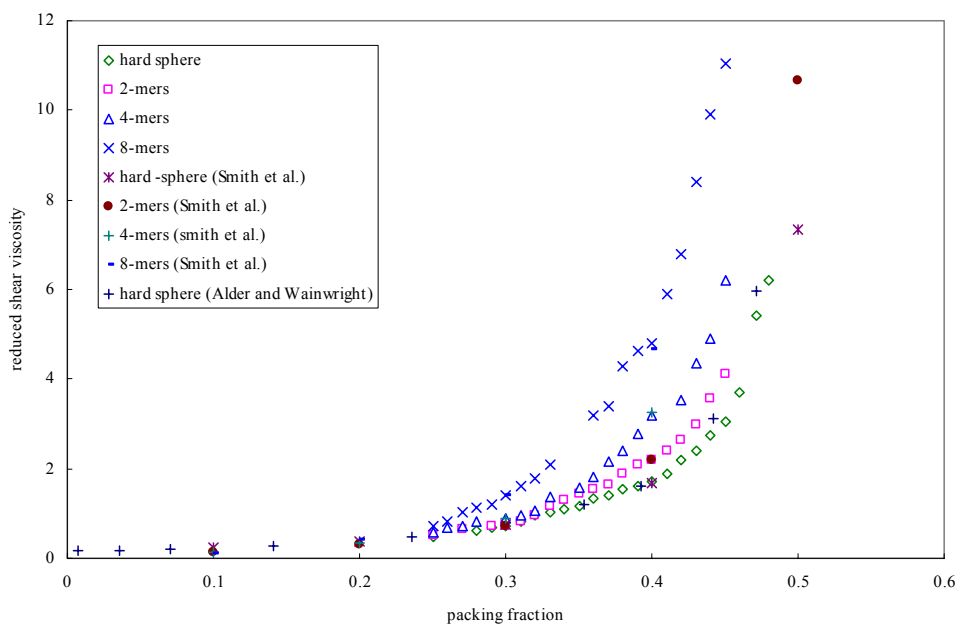


Figure 1 Reduced shear viscosity of hard sphere chain fluids as a function of packing fraction.

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