TRANSPORT PROPERTIES OF DENSE FLUID MIXTURES
USING NONEQUILIBRIUM MOLECULAR DYNAMICS

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S.Murad

Department of Chemical Engineering
University of Illinois at Chicago

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ABSTRACT

Computer Simulation Studies were carried out using the method of equilibrium and nonequilibrium molecular dynamics (NEMD) to examine a wide range of transport processes in both fluids and fluid mixtures. This included testing a wide range of mixing rules for thermal conductivity and viscosity. In addition a method was developed to calculate the internal rotational contributions to thermal conductivity and the accuracy of current methods for predicting these contributions were examined. These comparisons were then used to suggest possible ways of improving these theories.

The method of NEMD was also used to examine the critical enhancements of thermal conductivity. Finally, molecular simulations were carried out to study the various transport coefficients of fluids confined by membranes, as well as important transport processes such as osmosis, and reverse osmosis.

SUMMARY

1. An algorithm was developed and used to calculate the viscosity and thermal conductivity of continuous or polydisperse mixtures with various distributions (e.g. linear, several gaussian, unsymmetrical, etc.) using nonequilibrium molecular dynamics (NEMD). The results obtained were used to examine the several n-fluid characterizations possible. Our results showed clearly that the 2-fluid characterization was significantly better than the 1-fluid characterizations. In addition there was no real improvement in going to a higher order characterization e.g. a 3- or a 4-fluid characterization.

2. A method was developed to calculate the thermal conductivity of nonspherical (rigid) molecules using NEMD. It was shown that a straightforward extension of the spherical method is not correct. The technique was implemented and used to calculate the thermal conductivity of hydrogen chloride using several previously developed intermolecular potential models. These thermodynamic(static) properties based models were found to give reasonably accurate transport properties such as thermal conductivity. In addition all models appeared to give essentially the same results, perhaps showing that liquid transport properties are not as sensitive to the details of the intermolecular potentials.

3. We also completed a preliminary study of the viscosity of both pure diatomics and their mixtures (e.g. N_2 , Cl_2 , etc.). The results were used to examine a range of mixing rules available for such systems.

4. As, a prelude to studying transport properties of systems beyond diatomics, where molecular flexibility would be important, we completed a study of the various flexibility(vibrational) effects, such as bond bending, bond stretching etc, on linear and nonlinear model triatomics. To examine these effects we looked at the pressure second virial coefficients. Our results confirmed that "bond bending" is much

more important in such systems than "bond stretching". This will help us model more complicated systems more efficiently in the future.

5. A novel new technique for the computer simulation of fluids in various confined geometries, such as micropores was developed. A unique feature of the model is that it allows a gradual transition from impermeable to totally permeable confining walls, while maintaining their atomic nature. Atomically rough walls have been studied by others as well, but the models used do not allow for the permeability of the walls to the confined fluid to be controlled easily. The method is based on the conventional microcanonical (NVE) ensemble. The confining walls are formed by tethering (attaching) a subset of the molecules in the simulation system to suitable tether sites, using a potential such as the simple harmonic model. By choosing appropriate tethering sites, the confining walls can have any desired geometry.

We initially used the method to study density profiles, and the self-diffusion coefficients of fluids in slit micropores. These properties for such systems have been studied previously both theoretically and experimentally, and we were able to validate our model. More recently, and such studies are continuing, we have used this new method to study anisotropic diffusion and thermal conductivity coefficients, as a function of wall permeability, between the permeable and impermeable limits, using both equilibrium and nonequilibrium molecular dynamics. Our results have clearly indicated the strong anisotropy in both these transport coefficients (parallel and perpendicular to the pore walls), especially at low permeability values. Studies have so far been conducted on both monatomic and diatomic fluids.

Finally, we have also used this new technique to model a semi-permeable membrane wall, permeable to only the solvent in a solution. Our results have confirmed van't Hoff's famous relation for osmotic pressure in semi-permeable membranes over a wide range of concentrations. We have also examined the dynamics of permeation of the solvent molecules in such systems.

An understanding of fluids in confined systems is necessary for many processes such as chromatography, oil recovery catalysis, membrane separation technologies, etc. Since the pore size can approach molecular

dimensions, it is difficult to study these micropores materials experimentally. Computer simulations are an ideal tool to investigate such systems, because they are not subject to the usual experimental constraints of size, temperature, geometric complexity, etc.

6. We have proposed an improved method for predicting the contributions to thermal conductivity from internal rotational modes for polyatomic fluids and their mixtures. Most currently used predictive techniques such as TRAPP, assume these contributions to be density independent, and equate them to their zero density values, which can be approximated by, for example, the Eucken method. We carried out a series of studies using the method of nonequilibrium molecular dynamics (NEMD), to study the thermal conductivity, including the internal rotational contributions for model systems such as diatomics (N_2 , Cl_2), polyatomics (CH_4 , C_6H_6) and binary mixtures (both polyatomic-polyatomic, and polyatomic-monatomic). Our results showed that the internal rotational contributions are indeed density dependent, and vary from approximately 6 percent for diatomics, to almost 35 percent for more structured polyatomics such as benzene, while the remaining contributions come from the translational modes. The approximation of density independence of these contributions is therefore clearly in error, although in the case of diatomics, the overall effect is quite small. We also found that as a fraction of the total thermal conductivity, the internal-rotation contributions appeared quite insensitive to the density. We have therefore proposed that in making these predictions, a more appropriate approximation would be to obtain the fractional contribution from internal-rotational modes at the zero density limit, and assume this fractional contribution to be density independent. When compared with results from our NEMD simulations, such an approximation was usually within the estimated accuracy of the simulation, while the approximation of density-independent absolute contribution, currently being used could be off by upto an order of magnitude.

Our results also show why despite these shortcomings methods such as TRAPP have in fact been quite successful in predicting the thermal conductivity of systems such as hydrocarbon mixtures. In such systems the dominant contribution is from the translational modes. By using

semi-theoretical corrections (which such methods use), it is reasonably simple to rescale the translational contributions to account for the error in the rotational part. However, this may not be possible in more complex mixtures, and perhaps also explains why many of these theories fail for polar mixtures. We plan to investigate such systems next.

7. Using a method for studying continuous mixtures developed by us previously, we have investigated the thermal conductivity of continuous, semi-continuous, and discrete (multi-component) dense fluid mixtures. Several distributions including linear, symmetric and unsymmetric gaussian etc., were studied. These results were then used to evaluate various n-component characterizations for such mixtures. Our results consistently showed that a two-component characterization is significantly better than a one-component characterization for all distributions, continuous, or discrete. In addition, going to higher order characterizations (three or four component) did not improve results significantly.

We also found that the most efficient method for such characterizations for unsymmetric mixtures was to have each component represent an equal amount (in moles) of the mixture, rather than equal ranges of molecular parameters (e. g. for Lennard-Jones mixtures, ϵ , σ or M).

8. Using the method of NEMD, we have been able to demonstrate that in a model polar fluid (in our case a fluid with a central Lennard-Jones potential, plus point dipoles and quadrupoles), there is strong evidence of both heat induced birefringence (the spontaneous alignment of molecules along the direction of heat flow), as well the reciprocal effect of electric polarization upon thermal conductivity. In addition, we also found that an external electric field significantly changes the self-diffusion coefficients of such fluids, defined as one-third of the trace of the self-diffusion tensor.

The changes in the thermal conductivity and diffusion coefficients due to external electric fields are of considerable importance in many practical systems, such as, electric transformers. The transformer cooling fluid is polar, and is in a strong electric field.

9. We have also shown (this work is being carried out in collaboration with Dr. H. J. M. Hanley at the National Institute of Standards and Technology, and Professor D. J. Evans at the Australian National University) that critical enhancements in thermal conductivity can be studied using nonequilibrium molecular dynamics. This work has the potential of addressing many difficult problems in several theories, especially for mixtures.

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Ph.D DEGREES AWARDED

Khalid Mansour, Equilibrium and Nonequilibrium Properties Using Molecular Simulations.

Prasad Ravi, Thermal Conductivity of Fluids Using Non-equilibrium Molecular Dynamics

Barbara Holtz, Fluids Confined by Porous Membranes (University of Kent, Canterbury)