Decoupling of liquid thermo-physical properties using a nano-scale approach

James J. Cannon[1,2], Tohru Kawaguchi[3], Takashi Kaneko[3], Takuya Fuse[3], Junichiro Shiomi[2]
[1] Kyushu University, Dept. of Mechanical Engineering
[2]The University of Tokyo, Dept. of Mechanical Engineering
[3]DENSO CORPORATION

Thermal conductivity and viscosity are critical properties to consider when choosing a liquid for an application. Since they are coupled, improvement in one can result in deterioration in another. Consequently, it is desirable to learn why these are inter-related with a view to decouple them. With this aim, using glycol solution as an example, we have conducted a molecular simulation study to identify the structural features of the two properties that lead to inter-relation, and we identify hydrogen-bonding as an underlying mechanism by which independent control may be achieved.

Liquid mixtures are applied in a range of engineering applications, and the choice of liquid is strongly dependent on the required thermal conductivity and viscosity properties. These can be adjusted by varying the types of liquids and their ratio, however ideal properties are not often achieved because the properties are coupled, so improvement of one property can be accompanied by deterioration in another.

Subsequently, it is of great interest to investigate the origins of this inter-dependency. While the thermophysical properties are observed on the macro-scale, they have their origins on the nano-scale, driven by molecular structure and interaction, and therefore Molecular Dynamics (MD) simulation is a promising method of investigation. Subsequently, we perform an MD simulation study into the inter-relation of these two thermophysical properties.

As the basis for our study we choose to investigate a solution of ethylene glycol in water at 70wt% glycol (Fig. 1), since alcohol solutions are common in engineering applications. We validate the current model implementation by comparing against experiment, yielding a thermal conductivity of 0.49 W/m.K (compared to 0.34 W/m.K in experiment) and a viscosity of 5.5 mPa.s (compared to 5.6 mPa.s in experiment).

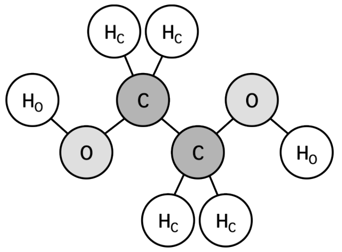

Fig. 1 Ethylene glycol molecule. Atoms are named as referred to in this manuscript.

In order to understand the relation of structure and thermophysical properties, glycol structural variation is employed. Here, small changes in bond-length and charge-distribution are induced, and the resulting change in properties measured. There are 5 control-variables; 4 types of bonds, each of which can be varied to alter the structure, as well as atomic charge variation, altering charge on the H_O atom with appropriate scaling of charges on the inner atoms (C and H_C) to ensure molecular neutrality is maintained.

We determine each thermophysical property as a quantitative function of structural changes. Using an L1 regularisation technique in the form of the Least-Absolute Shrinkage and Selection Operator (LASSO), we determine that thermal conductivity depends on C-C and C-O bond-length and charge-distribution, and while viscosity also depends on carbon-connected bonds, it is much more strongly dependent on the O-H_O bond length. Based on this understanding, one can construct a model based upon these principle features, and attempt to predict the thermophysical properties of molecules. Figure 2 shows excellent predictive capability based on these few principle features. The importance of O-H_O bond-lengths reveals the strong role of hydrogen bonding on viscosity.

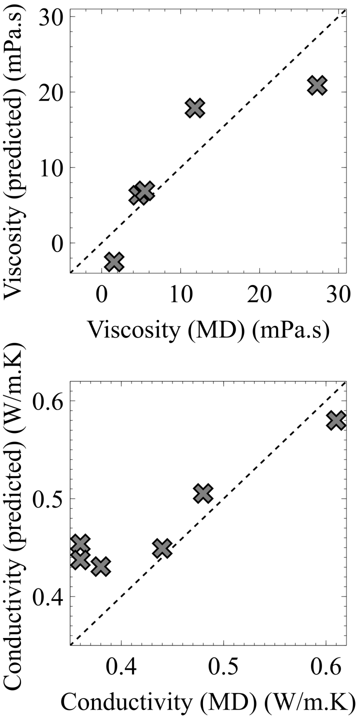

Fig. 2 Comparison of predicted viscosity (top) and thermal conductivity (bottom) against values obtained by molecular simulation. Excellent agreement can be observed in both cases, albeit with a slight over-estimation at lower values of thermal conductivity.

Work to be published in the International Journal of Heat and Mass Transfer 105 pp12-17 (2017)