



Understanding decoupling mechanisms of liquid-mixture transport properties through regression analysis with structural perturbation



James J. Cannon^a, Tohru Kawaguchi^b, Takashi Kaneko^b, Takuya Fuse^b, Junichiro Shiomi^{a,*}

^a Department of Mechanical Engineering, The University of Tokyo, Tokyo, Japan

^b DENSO CORPORATION, 500-1, Minamiyama, Komenoki-cho, Nisshin-shi, Aichi 470-0111, Japan

ARTICLE INFO

Article history:

Received 18 May 2016

Received in revised form 18 August 2016

Accepted 16 September 2016

Keywords:

Glycol
Mixture
Molecular dynamics
Optimization
Thermal conductivity
Viscosity

ABSTRACT

Optimization of liquid thermophysical properties is important for engineering applications; often achieved by mixing two or more liquids. An important issue is that properties tend to be coupled, which can be problematic if improvement of one property is accompanied by deterioration in another. Therefore, optimization is typically a compromise between properties, and it could be enhanced if they could be decoupled. Such decoupling however first requires an understanding of the common and distinct physical origins of each thermophysical property of interest. Here, we introduce a new approach to gain such understanding, combining molecular-simulation-based structural perturbation with regularized statistical analysis. Considering viscosity and thermal conductivity of a water–glycol mixture as a test-case, we identify the role of structure on each property, and highlight the important role that hydrogen bonding can play in such decoupling.

© 2016 Elsevier Ltd. All rights reserved.

1. Introduction

Pure liquids do not typically possess the ideal thermo-physical properties required for a given application, and therefore mixtures are often employed. By varying the ratios of the liquids, the properties can be tuned precisely. Unfortunately, improvement in one property can be accompanied by a deterioration in another, such as during addition of additives in nano-fluids for increased thermal conductivity (resulting in unwanted higher viscosity [1,2]) or addition of anti-freeze to water for lower freezing-temperature (with unwanted deterioration in thermal conductivity and viscosity). Consequently, it is of great interest to learn how to control each thermo-physical property independently. This can be achieved in two stages: Firstly, the physical origins of each thermophysical property of interest must be understood and any uniqueness and overlap (inter-dependencies) clarified. Secondly, the structure of the molecules employed must be such that the unique origins are accentuated and independent control becomes possible. Practically, this can be achieved by choosing liquid molecules with specific numbers, arrangements and bonding of atoms.

In this manuscript, we focus on the first stage, demonstrating a novel approach to understanding the inter-dependent and independent origins of two thermophysical properties; in this case vis-

cosity and thermal conductivity. We demonstrate how using non-physical structural variation can lead to useful physical insights into decoupling, and a greater understanding into the role of molecular structure in coupled and decoupled variation of each property. We employ a structural perturbation technique achieved through molecular simulation, coupled with regularized statistical analysis. Statistical optimization techniques have gained significant recent interest for the optimization of solid materials [3–8] but to our knowledge this is the first time a technique of this type has been applied in the field of liquid property optimization. The utility of this technique is demonstrated through application to a mixture of water and ethylene glycol at 70 wt% (0.4 glycol mole fraction). This mixture is chosen since it is a common mixture employed in anti-freeze applications and thus is of wide interest in industry.

2. Methods

Structural perturbation is performed both in terms of variation of the lengths of the 4 types of bonds ((H_o...O), (O...C), (C...C) and (H_c...C)) (see Fig. 1 for atom name definitions) as well as the charge distribution. These perturbations are permitted in combination (for example, changing the (C...C) and (H_o...O) bond-lengths simultaneously), and furthermore, we do not assume a linear relationship between the thermo-physical properties and control-variables: in this study up to a 3rd-order cubic relationship is

* Corresponding author.

E-mail address: shiomi@photon.t.u-tokyo.ac.jp (J. Shiomi).

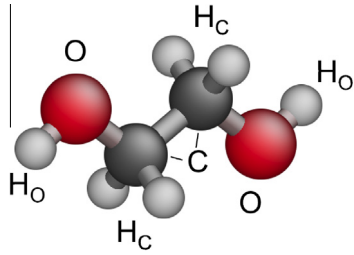


Fig. 1. Schematic of an ethylene glycol molecule with the atoms named as used in this manuscript.

permitted (for example, considering the relationship between the viscosity and the product of $(H_o \dots O)$ and $(C \dots C)^2$). Thus there are 55 linearly-independent features describing the parameter-space for each property, however only very few are expected to play an important role. In order therefore to reduce the dimensionality of the problem and identify the principle components, we employ L1-norm statistical regularization in the form of the Least Absolute Shrinkage and Selection Operator (LASSO) method [9]. Eq. (1) shows the typical cost function for least-squares linear regression (where the actual value of the property for structure i is denoted as y_i and is estimated based on a sum over all j features of the model, denoted x_{ij} weighted by coefficients β_j) with an additional term on the right side in the form of the LASSO regularization penalty. Put briefly, the LASSO method applies this penalty to the size of the feature coefficients, and the strength of this penalty is controlled by the value of α . A relatively high value of α will result in most feature coefficients being driven towards zero, and the remaining non-zero coefficients will be the principle features describing the property of interest (i.e., viscosity or thermal conductivity). For further details, the reader is directed to the work of Efron et. al. [9].

$$J = \sum_{i=1}^n \left(y_i - \left[\beta_0 + \sum_{j=1}^p \beta_j x_{ij} \right] \right)^2 + \alpha \sum_{j=1}^p |\beta_j| \quad (1)$$

The LASSO method essentially places the features in order of importance (the most important features having their coefficients being driven to zero last). Taking the features in order of importance, the first N features can be used in standard linear regression to build a predictive model. The value of N however must be decided, since too many features will result in over-fitting while too few features will result in a biased model unrepresentative of the problem. This is achieved by testing the ability of the model to predict data unused in the generation of the model, quantifying the difference in terms of the residual sum of squares. At the optimum balance between bias and over-fitting (i.e., optimum value of N), the predicted test-data properties will most-closely match the actual test-data properties, and this will be revealed by a minimum in the residual sum.

The bond-lengths are defined non-dimensionally in terms of the lengths relative to the original glycol model, so by this definition the original molecule has bond-lengths of 1. Charge (q) is meanwhile defined in a similar way, in terms of the charge on the outer (H_o) atom relative to the same atom in the original model, while charges on the inner C and H_c atoms are adjusted proportionally to maintain a neutral molecule. It can be noted that as in the original model, both the outer and inner atoms carry positive charge and the only negatively-charged atom is oxygen. Here we limit the maximum value of q so that the inner atoms remain non-negative for every calculation. Bond-length variation is performed between 0.6 and 2.0, while charge varies between 0.7 and 1.7 (the latter resulting in neutral inner-atoms).

The all-atom Szefczyk model [10] is employed to model ethylene glycol (Fig. 1) while the TIP4P/Ew model [11] is employed for water. The number of water and glycol molecules is held constant throughout this study. Approximately 356 molecules of glycol mixed with 525 molecules of water are used for thermal conductivity calculations, and four-times that for viscosity due to elongation of the box in one direction. The time-step employed is 0.5 fs for thermal conductivity and 2 fs for viscosity calculations, run for 3 ns and 10 ns respectively. Cut-off is 14 Å for short-range coulomb interactions and 12 Å for Lennard-Jones interactions. System temperature is set to 300 K and system pressure to 1 atm, achieved first through equilibration under constant temperature and pressure. For thermal conductivity calculations, equilibration is performed for a further 100 ps in a micro-canonical ensemble, before continuing to be run under this ensemble during measurement. Viscosity is calculated using periodic non-equilibrium forcing [12] with a cosine acceleration of 0.025 nm/ps², low enough to ensure equilibrium temperature and pressure conditions are maintained [13]. The volume is held constant during measurement, while a thermostat is employed to prevent heating from the non-equilibrium driving force.

Thermal conductivity is calculated using the Green-Kubo approach [14,15] based on the time-correlation integral of the flux. The flux (Eq. (2a)) itself can be broken into a virial (interactive) term J_v (Eq. (2b)) and convective term J_c (Eq. (2c)).

$$VJ = V(J_v + J_c) \quad (2a)$$

$$J_v = \frac{1}{2} \sum_{i=1}^N \sum_{a=1}^{n_i} \sum_{j=1}^N \sum_{b=1}^{n_j} \mathbf{r}_{ij}^{com} \mathbf{f}_{ia,jb} \cdot \mathbf{v}_{jb} \quad (2b)$$

$$J_c = \sum_{i=1}^N \mathbf{v}_i^{com} e_i - \sum_{v=1}^M h_v \sum_{i=1}^{N_i} \mathbf{v}_{i_v}^{com} \quad (2c)$$

The virial term considers interactions between molecules i and j , summing over all molecules N and all n_{ij} atoms within each molecule. The terms \mathbf{r}_{ij}^{com} , $\mathbf{f}_{ia,jb}$ and \mathbf{v}_{jb} correspond to the center-of-mass separation of atoms i and j , force between atom a on molecule i and atom b on molecule j and the velocity of atom b on molecule j , respectively. The first term of the convective contribution meanwhile sums the product of the center-of-mass velocity \mathbf{v}_i^{com} of each molecule and its internal energy e_i over all N molecules. A second (enthalpic) term is subtracted from this. Here, there is a double-sum over all M species in the liquid of the partial enthalpy h_v of species v , and the center-of-mass velocities of the molecules of species v , $\mathbf{v}_{i_v}^{com}$.

It is well-known that heat-flux in liquids is dominated by the virial term and that the convective term is relatively insignificant [16], and this is also observed in all our calculations. Furthermore, given the large number of data points required for statistical analysis, since the enthalpic term either requires extra NVT-ensemble simulations or additional pressure computation it would be helpful if this term could be neglected. In order therefore to gauge the extent of the influence of the enthalpic term on the overall thermal conductivity, the partial enthalpy was calculated using separate NVT-ensemble simulations, by taking the 70 wt% system and calculating its enthalpy with up to ± 5 Water or Glycol molecules. This then permitted the partial enthalpy to be calculated by the simple relation $h_x = (\delta H_x / \delta N_x)_{N,\beta,P,T}$, giving values of -40.3 kJ/mol and -44.2 kJ/mol for water and glycol respectively. That they only differ by 10% underlies the near-ideal nature of the two liquids. Calculation of thermal conductivity with and without the enthalpic term subsequently shows no difference within the precision of thermal conductivity values reported (2 decimal places in units of $\text{Wm}^{-1} \text{K}^{-1}$) and so it can be safely excluded from the calculations performed here.

Download English Version:

<https://daneshyari.com/en/article/4994666>

Download Persian Version:

<https://daneshyari.com/article/4994666>

[Daneshyari.com](https://daneshyari.com)