TOWARDS PREDICTION OF OPTIMAL ALCOHOL ANTIFREEZE STRUCTURAL FEATURES USING THE EXTREME GRADIENT BOOSTING METHOD WITH OPTIMIZATION

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a Thesis Presented for the Degree of

Bachelor of Engineering

九州大学

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August, 2019

Acknowledgements

I am thankful for being a member of this project, for the people that I have been with and cooperate and for the experience i have gained professionally and individually that support my self development

I owe my appreciation to Prof. James J Cannon for being an understanding advisor, a friend and an important teacher. I am thankful to him for providing me a freedom of research environment, a chance to explore myself professionally and personally, for providing me personal advices when I was in crises and for letting me try my most non-sense ideas.

I send my gratitude to Prof. Hiroshi Takamatsu for accepting me into this laboratory, for being personally and professionally supportive by constructive critisms and advices that I would never think of without him, for sharing me his favourite drink and for showing me the world of research.

I am grateful to Prof. Kurata and all of former and current Heat and Mass Transfer laboratory members that I have met, for being so kind, for helping me blend in the culture difference, for all of the professional advices and for giving me unforgettable memories.

I greatly appreciate my best friend Tuan Do for all of his support in my personal and professional life. Without his lessons, I could not have been able to finish this

work. Without his mid-night talks, I could have quit mid-way because of depression and lost of direction.

I am also lucky to have wonderful friends in my IUPE (G30) program for always supporting me through my hard times and for being a part of my memorable university life.

Finally, I owe my greatest appreciation to my family, my father, my mother, my sister and my cousin for being the strongest mental support and for trusting me, giving me a chance to be who i am today.

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Abstract

TOWARDS PREDICTION OF OPTIMAL ALCOHOL ANTIFREEZE STRUCTURAL FEATURES USING THE EXTREME GRADIENT BOOSTING METHOD WITH OPTIMIZATION

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In this research, we used a statistical approach to find a research direction as well as to predict structural features of the next generation of alcohol coolant, studying from 8 types of alcohol: methanol, ethanol, ethylene glycol, 1-propanol, 2-propanol, glycerol, 1,3-propanol and propylene glycol. The statistical approach is done by implementing a supervised machine learning technique named extreme gradient boosting while the experimental data for the statistical technique is obtained from the Green-Kubo relation based molecular dynamics simulations.

The results showed that the machine learning models can predict values from what they have learned. However, the models could not perform well for the data that has a different pattern than the training data. The results also suggest that to solve

this problem, these 2 solutions should be taken in action: diversify the training data and conduct research on special alcohol types.

The machine learning approach can also show the influence of structural features on thermal conductivity and viscosity, which from that further research can be conducted to examine the underlying mechanism of those features.

The optimization part successfully predicted the structural features of the next potential candidate from the given alcohol sample. However, a future improvement of variable set and an interpreting method need to be developed in order to construct a complete molecular structure.

Chapter 1

Introduction

1.1 Research Background

Choice of a cooling system is inevitable in many applications since the involvement of heat transfer is important in many industries such as automobiles, architecture and electronics. The cooling system plays an important role in managing the system temperature, preventing the operating system from being overheated, which could lead to severe consequences if it is not taken seriously. Compared to the development of cooling technologies, the development of the cooling medium itself is often less considered. The choosing of an appropriate coolant would improve the performance as well as reduce cost for building the system.

Among liquid coolants, water is considered to be one of the best candidates for coolants with its high heat capacity and low viscosity (Mohapatra & Loikits, 2005). However, the temperature range of water in the form of liquid is only from 0°C to 100°C, which is a relatively small range. If the system temperature gets out of the range, the expansion of ice or the evaporation of vapor could cause unexpected

behaviors, which can lead to the break down of the entire system.

One of the ideas to overcome this problem is to create an aqueous-based solution with an alcohol to expand the operational temperature range while keeping the good performance in heat transfer and low viscosity. Many alcohol types have been introduced for this approach, such as propylene glycol, ethylene glycol, methanol or ethanol. However, their low thermal conductivity as well as high viscosity become a burden for the cooling medium. Thus, the finding of new alcohol in cooling is necessary. However, while there are an enormous number of possibilities, the cost of conducting an experiment is not neglectable, not to mention that we do not have a clear direction to research towards the goal.

Such problems can be overcome if we can create functions that link molecular structure features to the values of desired properties such as thermal conductivity and viscosity. With such a function, we can adjust any structural feature to obtain corresponding property values as well as study further on existing database, we can be correctly oriented to reach the optimal coolant that satisfy all the desired property constraints.

Such functions can be obtained with the help of computational power such as molecular dynamics simulations and supervised machine learning. In this work, we develop a methodology that help us get a research direction as well as predict the molecular structural features of next-generation alcohol coolants for future antifreeze development using molecular simulation code LAMMPS for computer simulations combined with supervised machine learning using the eXtreme Gradient Boosting technique.

1.2 Why use computational methods?

To understand why computational power is such a perfect vehicle to deliver the answer for this problem, we will introduce the two computational techniques and how can they bring great benefits for this type of problem.

1.2.1 Supervised machine learning method

Supervised machine learning is a class of advanced computing and statistical techniques that maps a function of given sets of input-output. In other words, if the input is information of structural features and the output is desired properties, we can obtain the function that we desired as mentioned earlier. This is a highlight of implementing the computational method since conducting the function by analytical method would take a great amount of time and effort, not to mention the difficulty. However, using supervised machine learning requires a large amount of data in order to obtain accurate and acceptable results. Thus, the perfect combination for machine learning is molecular dynamics simulations.

1.2.2 Molecular Dynamics simulation

Molecular dynamics simulation is a computational system that numericalizes features and behaviors of atoms and molecules. We will discuss the details of molecular dynamics in the next section while here I will give some details of notable advantages of molecular dynamics in relation to this problem. Compared to manual experimental methods, molecular dynamics simulations brings much greater benefits.

Molecular dynamics simulations require information of the environment, such as

system volume, temperature, pressure and numerical information of investigated coolants, and appropriate computational power to conduct an experiment and calculate thermophysical properties. In that sense, it is much safer and precise in terms of environment control as well as simpler in terms of experimental setup, which saves a lot of resources.

By being able to control the process to every single detail, we also can have a more insight of atomic behaviors inside the system, in spite of the difficulty of observing it if we conduct the experiment traditionally.

Standing out from the above benefit, simulations can significantly reduce the time to conduct experiments. The entire process is automated with the human factor as an observer which allows the experiments to run continuously, avoiding the gap that exists in traditional experiments due to human body limitation, yet, without compromising the accuracy. To elevate this ability, simulations also can run in parallel, which means we can conduct several experiments at the same time; the number depending only on the available computational power; and the accuracy is still guaranteed.

Thus, we can escalate the number of experiments and get much greater amount of data with much shorter time to serve the machine learning purpose.

1.3 Thesis Outline

The thesis is presented in the following manner:

Chapter 1 - Introduction

Providing the background of the research, the idea to tackle the problem that we want to answer as well as the reason why we have that idea, an introduction about why computational methods should be applied to solve this problem.

Chapter 2 - Theory

Providing information of background knowledge that we need to know in order to understand the approach that we are about to propose. The background knowledge includes the Green-Kubo formulas of thermal conductivity and viscosity, molecular dynamics simulations, and all the relevant machine learning related techniques.

Chapter 3 - Method

Providing information of how to operate the approach in detail, including cultivating data method and data processing method.

Chapter 4 - Results and Discussion

Providing the results of models in different situations, the results from optimization process and discussion about the results.

Chapter 5 - Conclusion

Summary the entire work.

Chapter 2

Theoretical Background

To be able to understand the method, we will introduce a few theoretical backgrounds that are related to the tools I will use in this research.

2.1 Molecular Dynamics Simulation

As mentioned in the previous chapter, molecular dynamics simulation is a numerical system that describe atomic status over time in a specified environment. From the cultivated information, we can either investigate the atomic behaviors or calculate thermophysics properties such as thermal conductivity and viscosity easily. A standard molecular dynamics simulation has an algorithm as follows (Manjunatha, 2018)

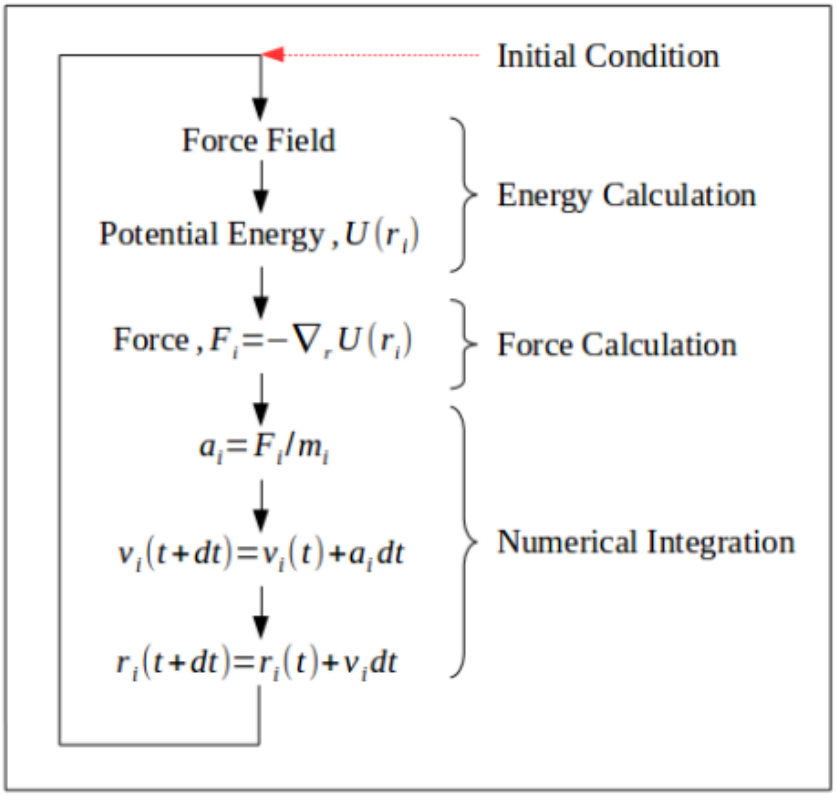


Figure 2.1: Basic outline of a MD simulation

The initial conditions describe the initial state of the atoms such as velocity $v(t_0)$, mass of atom m and coordination $r(t_0)$. For atoms of a liquid, given the i^{th} atom, the initial coordination $r_i(t_0)$ is randomized along with several constraints such as structural constraints (angles, bond lengths) and displacement constraints to avoid malfunction in the system as well as systematic errors. The initial velocity $v_i(t_0)$ is randomized on the Gaussian distribution with the constraint that the total momentum of the entire system is 0.

After the initial setup, a class of functions called a force field is used to calculate the potential energy $U_i = U(r_i)$ which is a function of position that obeys the structural constraints of the atom. The obtained potential energy $U(r_i)$ can be used to deduce the forces F_i that apply on the atom.

The force F_i is then processed by using Verlet algorithm as follows to obtain the functions of velocity and position over time. For a time step Δt, the function that presents the position of the i^{th} atom after Δt is

$$r_i(t + \Delta t) \approx r_i(t) + \Delta t \dot{r}_i(t) + \frac{1}{2}\Delta t^2 \ddot{r}_i(t) \tag{2.1.1}$$

To get the velocity term after a time step Δt, we have to deduce $r_i(t)$ backwards from $r_i(t + \Delta t)$. Thus

$$r_i(t) \approx r_i(t + \Delta t) - \Delta t \dot{r}_i(t + \Delta t) + \frac{1}{2}\Delta t^2 \ddot{r}_i(t + \Delta t) \tag{2.1.2}$$

Substituting 2.1.2 into 2.1.1 we get

$$\dot{r}_i(t + \Delta t) = \dot{r}_i(t) + \frac{1}{2}\Delta t \left[\ddot{r}_i(t) + \ddot{r}_i(t + \Delta t)\right] \tag{2.1.3}$$

Or

$$\dot{r}_i(t + \Delta t) = v_i(t + \Delta t) = v_i(t) + \frac{1}{2m_i}\Delta t \left[F_i(t) + F_i(t + \Delta t)\right] \tag{2.1.4}$$

The values of positions and velocities at $t + \Delta t$ will be served as the next initial condition for the next loop of calculation until the set running time T is reached. The values of positions and velocities will be used to calculate thermal conductivity and viscosity by using a deduction of the Green-Kubo relation.

2.2 Green-Kubo Relation

Green-Kubo relation is a formula that shows the relationship between the transport coefficient and the dynamical variables. The general expression is as follows (Hansen & McDonald, 2013)

$$K = C \int_0^\infty \langle D(t)D(0)\rangle \mathrm{d}t \tag{2.2.1}$$

Where K is the transport coefficient, D is dynamical variable terms and C is the function constant. To be able to calculate viscosity and thermal conductivity values, the Green-Kubo expression will be transformed, without detailed derivation delivered, and presented as follows

2.2.1 Viscosity

The Green-Kubo expression for calculating viscosity is as follows:

$$\eta = \frac{V}{k_b T} \int_0^\infty \langle P_{\alpha\beta}(t) \cdot P_{\alpha\beta}(0) \rangle \, dt \tag{2.2.2}$$

Where P is stress tensor terms, $\alpha, \beta \in (x, y, z)$ is the 3D direction, V is the system volume, T is the system temperature, $k_B = 1.38 \times 10^{-23}$ $[m^2 \cdot kg \cdot s^{-2} \cdot K^{-1}]$ is the Boltzmann constant and $\langle\rangle$ is the ensemble average (Hansen & McDonald, 2013). Furthermore, the stress tensor terms can also be expressed as follows:

$$P_{\alpha\beta} = \frac{1}{V} \left(\sum_i m_i v_{i_\alpha} v_{i_\beta} + \sum_i r_{i_\alpha} f_{i_\beta} \right) \tag{2.2.3}$$

Where m is the atom mass, v is the atom velocity, r is the atom position, f is the forces act on atom and i is the atom index (Allen & Tildesley, 2017).

2.2.2 Thermal Conductivity

The Green-Kubo expression for calculating thermal conductivity is as follows:

$$\lambda_T = \frac{V}{k_{\mathrm{B}} T^2} \int_0^\infty \mathrm{d}t \, \langle J_\alpha(t) J_\alpha(0) \rangle \tag{2.2.4}$$

Additionally, J is heat flux terms, V is the system volume, T is the system temperature, $k_B = 1.38 \times 10^{-23}$ $[m^2 \cdot kg \cdot s^{-2} \cdot K^{-1}]$ is the Boltzmann constant, $\langle\rangle$ is the

ensemble average and $\alpha \in (x, y, z)$ is the 3D direction (Hansen & McDonald, 2013). Furthermore, The heat flux terms can be broken down further. Thus,

$$J_\alpha = \frac{1}{V}\left(\sum_i e_i v_i + \sum_{i<j} \left(f_{ij} \cdot v_j\right) r_{ij_\alpha}\right) \tag{2.2.5}$$

Where e is energy per-atom, v is the velocity of atoms, f is the force between atoms, r is the distance between atoms in the α direction and i and j are the atom indices (Manjunatha, 2018).

2.3 eXtreme Gradient Boosting Method

eXtreme Gradient Boosting (XGBoost) method is a robust supervised machine learning method that consists of different advanced statistical techniques. The advanced statistical techniques help XGBoost achieve a high calculation speed and accuracy. To be able to understand XGBoost for the purpose of this research, the following XGBoost component techniques will be explained

- Gradient boosting
- Regularization object
- Sub-sample & sub-column

2.3.1 Gradient Boosting

The gradient boosting feature improves the accuracy of model prediction ability and calculation speed. Gradient boosting consists of 2 parts: boosting and gradient.

Boosting

From a mathematical perspective, the boosting algorithm is similar to the Lagrange Multiplier method. Given a sample data set of n elements to make the XGBoost model, the mission of boosting is to minimize the loss function $\sum_{i=1}^{n} l\left(y_i, \hat{y}_i\right)$, which is the total sum of differences between predicted values and actual values, so that the predicted outcomes are closest to the actual values. The boosting algorithm also involves creation of multiple sub-functions from given variables which serve as constraints for the Lagrange problem. Finally, boosting algorithm takes an adjustable coefficient as the Lagrange Multiplier coefficients. Instead of having many coefficients as is typically used in the Lagrange multiplier method, boosting only uses a unified coefficient to avoid unnecessary complexity for the system while it does not have to compromise too much on accuracy. The boosting algorithm can be represented by the following expression, where $\hat{f}_b(x)$ represents each sub-function that boosting creates and λ represents the Lagrange coefficient:

$$0 \leftarrow \sum_{b=1}^{B} \sum_{i=1}^{n} l\left(r_i, \hat{r}_i\right)_b + \sum_{b=1}^{B} \lambda \hat{f}_b(x) \tag{2.3.1}$$

Which can be written as:

$$0 \leftarrow \sum_{i=1}^{n} l\left(y_i, \hat{y}_i\right) + \sum_{b=1}^{B} \lambda \hat{f}_b(x) \tag{2.3.2}$$

Furthermore, B is the total number of sub-functions, n is the number of data in the sample data and r is the difference between actual values and predicted values of the previous sub-function. For example, for any data point i in the data sample being processed by sub-function b: $r_i^b = y_i^{(b-1)} - \hat{y}_i^{(b-1)}$. Initially, $r_i^0 = y_i$ (James, Witten, Hastie, & Tibshirani, 2013).

Gradient

Instead of $\sum_{i=1}^{n} l\left(y_i, \hat{y}_i\right)$, the loss function is expanded by the Taylor expansion to the second degree, which is where the terms "gradient" comes from. Thus, at any t^{th} sub-function, the loss function becomes:

$$\sum_{i}^{n_t} \left[l\left(r_i, \hat{r}_i^{(t-1)} + \hat{f}_t\left(x_i\right)\right)\right] \tag{2.3.3}$$

$$\sum_{i=1}^{n_t} \left[l\left(r_i, \hat{r}^{(t-1)}\right) + g_i \hat{f}_t\left(\mathbf{x}_i\right) + \frac{1}{2} h_i \hat{f}_t^2\left(\mathbf{x}_i\right)\right] \tag{2.3.4}$$

Where $g_i = \partial_{\hat{r}^{(t-1)}} l\left(r_i, \hat{r}^{(t-1)}\right)$ and $h_i = \partial^2_{\hat{r}^{(t-1)}} l\left(r_i, \hat{r}^{(t-1)}\right)$ are the Taylor expansion coefficients. By expanding into 2nd degree of Taylor expansion, the loss function will converge faster and more accurately while avoiding overfitting (Chen & Guestrin, 2016).

Overfitting refers to the performance of a model that is particularly good for a specific set of data and consequently may not be able to produce reliable predictions.

2.3.2 Regularization Object

Regularization is a technique that identifies unnecessary or less important variables by shrinking the coefficient of all variables (the coefficients inside the sub-functions, which are different from the Lagrange coefficient) towards zero. The coefficients of unnecessary or less important variables will become zero, thus, do not affect the model (James et al., 2013). To control the regularization process, the XGBoost method has 2 parameters, the LASSO parameter (Tibshirani, 1996) and the Ridge Regression parameter (Hoerl & Kennard, 1970).

2.3.3 Subsample & Subcolumn

Machine learning techniques normally use a set of sample data (training data) to create the component functions. However, using the entire training data set often encounters overfitting problems. Thus, XGBoost introduces sub-sample and sub-column features.

Sub-sample is a technique that instead of using the entire training data set, the algorithm only uses a portion of it. Sub-column is similar to sub-sample but instead of using a part of training data, the algorithm uses a subset of the available variables. Thus, for each sub-function, a different set of sub-sample and sub-column will be implemented. By doing so, the algorithm can prevent overfitting and detect the relationship between variables and outcomes even further and use of sub-columns also increase the computing speed (Chen & Guestrin, 2016).

Corresponding to the explained theory, XGBoost has the following parameters that need to be chosen:

- n_estimators = number of sub-functions B

- learning_rate = the Lagrange coefficient λ

- subsample = sub-sample size

- colsample_bytree = sub-column size

- reg_alpha = the LASSO parameter

- reg_lambda = the Ridge Regression parameter

2.4 Cross Validation

Every predictive model for a purpose comes along with a prediction error (true error), which show how different the outputs of the model compared to the true values of the corresponding inputs. Cross validation is a method that estimates the true error of a predictive model. For sample data, which includes both input and true values of output, the estimation of error is a simple job. However, for real data, the true error is usually unable to be found due to the absence of the true values of output. Thus, cross validation is implemented to approximate the true error from existing data sets (Rodriguez, Perez, & Lozano, 2010).

k-folds method

The k-folds method is a cross validation method that's popularly used in machine learning because of its good performance. In the k-fold method, the sample data set of n data points is divided into k equal $\frac{n}{k}$ data point portions with no shared component. The ith portion will be used to test the model (validation set) and give a numerical test error while the other k-1 portions will be used to train the model (training set). The process iterates k times so that every portion would be selected as test set once. The true error of the model will be estimated by averaging k numerical values of test error. The error measuring error for numerical output problem can be mean square error method as follows:

$$MSE = (y - \hat{y})^2 \tag{2.4.1}$$

Where y is the real value and $\hat{y}$ is the predicted value. Thus, the true error estimation becomes

$$TrueErrorEstimation = \frac{1}{k}\sum_{i=1}^{k}\sum_{j=1}^{n_i}(y_j - \hat{y}_j)_i^2 \tag{2.4.2}$$

Where i is the index of divided portions, j is the index of data points and n_i is the data in the i^{th} portion. The k-folds method helps us to reduce the variance of models' training scores, which due to the splitting of validation set and training set, and estimate the most stable performance scores.

Chapter 3

Method

In this work, we will investigate alcohol-water mixtures of 8 different alcohols with the solution concentrations varying from 2% to 50% for each. The investigated alcohols include:

- ethylene glycol
- ethanol
- methanol
- glycerol
- 1-propanol
- 2-propanol
- 1,3-propanediol
- propylene glycol

as they are alcohol types that were used as industrial antifreeze. The methodology is operated according to the following diagram

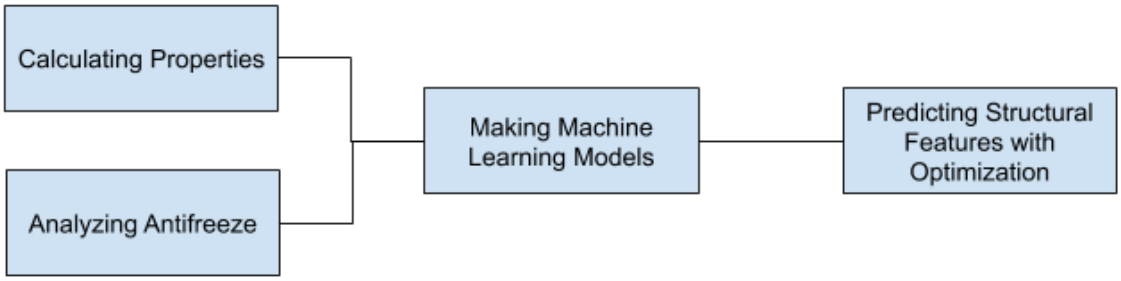


Figure 3.1: Procedure of the Methodology

3.1 Calculating Properties

In this work, the calculations of properties are carried out by LAMMPS (Plimpton, 1995). Since the investigated objects are water-alcohol mixtures, the fundamental inputs include

- Number of alcohol molecules

- Number of water molecules

- Declaring implemented alcohol molecular model

- System temperature T

- System volume V

- System pressure P

TIP4P/Ice (Abascal, Sanz, García Fernández, & Vega, 2005) will be used as the water model throughout all mixtures while all alcohol models are based on OPLS-AA (Jorgensen, Maxwell, & Tirado-Rives, 1996), which is derived from the Optimized Potentials for Liquid Simulations models (Jorgensen & Tirado-Rives, 1988).The system pressure is set at 1 atm while the volume of the system is set at 40x40x40 $Å^3$ throughout all simulations.

Since we are investigating throughout the mass concentration of mixtures, we construct a small converter that approximate the number of alcohol molecules and

water molecules from input mass concentrations. Assuming that the sum of volume of water and volume of alcohol equals the system volume, we obtain the following:

$$m_w = \rho_w V_w \tag{3.1.1}$$

$$m_w = \rho_w \left(V - V_{alc}\right) \tag{3.1.2}$$

$$m_w = \rho_w \left(V - m_{alc}/\rho_{alc}\right) \tag{3.1.3}$$

Where m_w is mass of water, ρ_w is density of water, V_w is volume of water, m_{alc} is mass of alcohol, ρ_{alc} is density of alcohol and V_{alc} is volume of alcohol.

But then the mass concentration is:

$$c_{\%} = \frac{m_{alc}}{m_{ak} + m_{alc}} \tag{3.1.4}$$

Thus

$$m_{alc} = \frac{c_{\%}}{1 - c_{\%}} m_w \tag{3.1.5}$$

Substitute 3.1.5 into 3.1.3 we obtain

$$m_w = \rho_w \left(V - \frac{c_{\%}}{1 - c_{\%}} m_w/\rho_{alc}\right) \tag{3.1.6}$$

Collect all the terms that contain m_w into one side then eliminate the coefficients, we obtain:

$$m_w = V \rho_{alc} \rho_w \left(1 - c_{\%}\right) / \left(\rho_w c_{\%} + \left(1 - c_{\%}\right) \rho_{alc}\right) \tag{3.1.7}$$

$$m_{alc} = \frac{1 - c_{\%}}{c_{\%}} m_w \tag{3.1.8}$$

Thus, the number of alcohol molecules N_{alc} and the number of water molecules N_w can be obtained as follows:

$$N_{alc} = N_A \frac{m_{alc}}{M_{alc}} \tag{3.1.9}$$

$$N_w = N_A \frac{m_w}{M_w} \tag{3.1.10}$$

Furthermore, N_A is the Avogadro number, M_{alc} is the molar mass of alcohol and M_w is the molar mass of water.

The method is validated by taking the calculated number of molecules to calculate the mass concentration. The error between calculated mass concentrations and input concentrations do not surpass 2%. Thus, the method is valid. The error arises from the fact that an integer number of molecules is required.

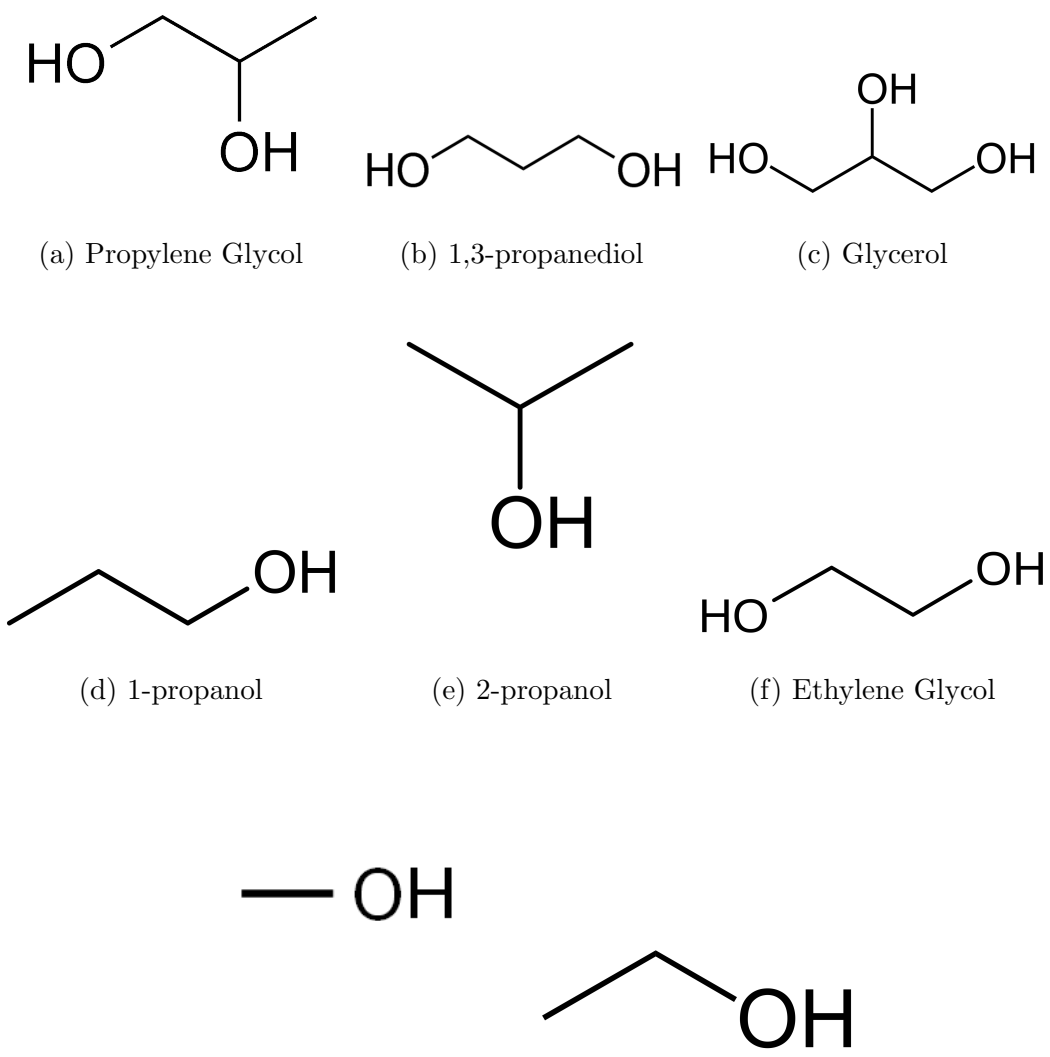
The densities of pure liquid are taken from online chemistry database CHERIC (Chemical Engineering and Materials Research Information Center) under conditions of 1 atm and 293K. Thus, the temperature of systems are set at 293K and 1 atm pressure.

The thermal conductivity can be deconstructed into 2 terms: virial and convective. The virial terms represents the interatomic interaction contribution to the thermal conductivity while the convective terms show the diffusion in the thermal conductivity. It is shown that the virial terms dominate the convective terms and can be used to represent the trend of values (Lin, Hsiao, & Chieng, 2011). Furthermore, in LAMMPS, the calculation time of the virial terms is much shorter compared to the total thermal conductivity due to the absence of the enthalpy quantity that is required to calculate the total term. Since the main aim of this work is the trend of values instead of the absolute values themselves, to reduce calculation costs, only the virial term is calculated. However, we can still calculate the total terms for viscosity since we do not need enthalpy quantity for viscosity calculations.

3.2 Analyzing Antifreeze Molecules

Since the purpose is to make a function of structural features to desired properties, in this section, we will discuss about which features should be chosen as variables for the functions. The variables' roles are not only to form relationships to desired properties, but also to distinguish different data points. To avoid unnecessary complexity, the variables (or structural features) should be independent.

In alcohol, it is already understood that the number of OH groups significantly affect the ability of heat transfer while the position of the OH group also change the properties values (Manjunatha, Takamatsu, & Cannon, 2017). However, there might be also other potential structural features that are left uninvestigated. Since we only care about the impact of the structural features on the thermophysical properties, we will select all the features that define an alcohol molecular structure.



(a) Propylene Glycol (b) 1,3-propanediol (c) Glycerol

(d) 1-propanol (e) 2-propanol (f) Ethylene Glycol

(g) Methanol (h) Ethanol

Figure 3.2: Molecular Structures of Sample Alcohol Types

As we can see, there are not many significant differences and are a lot of similarities across the molecular structures of all the selected alcohols. Thus, to distinguish different alcohols, the following features (in a molecular structure) will be used:

- Number of oxygen atoms

- Number of carbon atoms

- Number of single bonds, which also represents the number of hydrogen atoms

- The length of the main carbon chain

- The position(s) of the hydroxyl group(s)

To differentiate between different mixtures, the following features will be used:

- Number of water molecules

- Number of alcohol molecules

We can also see that glycerol is the only alcohol type that possess 3 hydroxyl groups while propylene glycol is really close to 1,3-propanediol (only different in the position of the 2nd hydroxyl group). Meanwhile, ethanol is quite similar to methanol and 1-propanol is a structural isomer of 2-propanol. Interestingly, among all the above alcohol types, methanol is the only type that is less viscous than water.

3.3 Machine Learning Implementation

Two sets of data will be prepared: a training data set and a testing data set. The training data set is used to construct the model while the testing data set is left unused throughout the training process and only used in approximating the true error so that the model is not overfit. We will make a model of thermal conductivity and a model of viscosity.

The parameter set for each model are decided by using k-fold methods. Within the possible range of parameters, every combination of parameters is cross-validated using the k-fold methodology and then the training performance scores are compared. The parameter set of the model that has the best training performance score will be chosen. The selected parameter sets will be used to create the models with the training data set. The constructed models will then be tested on the testing data set to obtain the performance score.

To thoroughly analyze the machine learning implementation, the training data set and testing data set will be decided by 2 ways: random and out of sample. The random method is to randomly divided the entire data set into the training data set and the testing data set and create the models. The resulting models will be used to progress to the final step. The out of sample method is to completely exclude an alcohol type out of the training sample. Four alcohol types, namely propylene glycol, methanol. 2-propanol and glycerol, will be in turn excluded to assess the characteristics of machine learning approach in this problem.

The performance score of the testing and training processes will be calculated using the R^2 score method as follows:

$$R^2 = 1 - \frac{SSR}{TSS} \tag{3.3.1}$$

Where

$$SSR = \sum_{i=1}^{n} \left(y_i - f\left(x_i\right)\right)^2 \tag{3.3.2}$$

$$TSS = \sum_{i=1}^{n} \left(y_i - \frac{1}{n}\sum_{j=1}^{n} y_j\right)^2 \tag{3.3.3}$$

Furthermore, SSR stands for squared sum of residual, TSS stands for total squared sum, y is the real value, $f(x_i)$ is the predicted value, n is the number of data in the data sample and i and j are data indices.

3.4 Optimization

In the optimization step, I will find the optimal values of desired properties while returning the corresponding inputs, which is the structural features in this work. The finding is done by setting up an optimization problem with an objective function

and different constraints. The objective function guides the computer to find the optimal results while the constraints help us to remove the unrealistic outcomes. This work considers optimization of thermal conductivity and viscosity. Thus, the problem will be described as follows:

Maximize:

$$\alpha \frac{TC - \overline{TC}}{\sigma_{TC}} - \beta \frac{Visc - \overline{Visc}}{\sigma_{Visc}} \tag{3.4.1}$$

Subject to:

- The number of alcohol molecules > 0

- The number of carbons and oxygens > 0

- The position of OH groups > 0

- The length of the main carbon chain $<$ the number of carbons

- The number of total molecules < 2100 (estimated number that fits in the investigated volume)

- Every input is integer

Where α and β are the weighting factors that define the importance of the thermal conductivity and viscosity. In this research, we value the thermal conductivity and the viscosity equally, which means $\alpha = \beta = 1$. σ_{TC} is the standard deviation of the sample thermal conductivity values, σ_{Visc} is the standard deviation of the sample viscosity values, $\overline{TC}$ is the mean of the sample thermal conductivity values and $\overline{Visc}$ is the mean of the sample viscosity values. The values of thermal conductivity and viscosity will be first standardized before processed in the objective function 3.4.1.

Chapter 4

Results and Discussions

4.1 Simulation Results

The calculated properties from Molecular Dynamics simulations are presented in the following forms

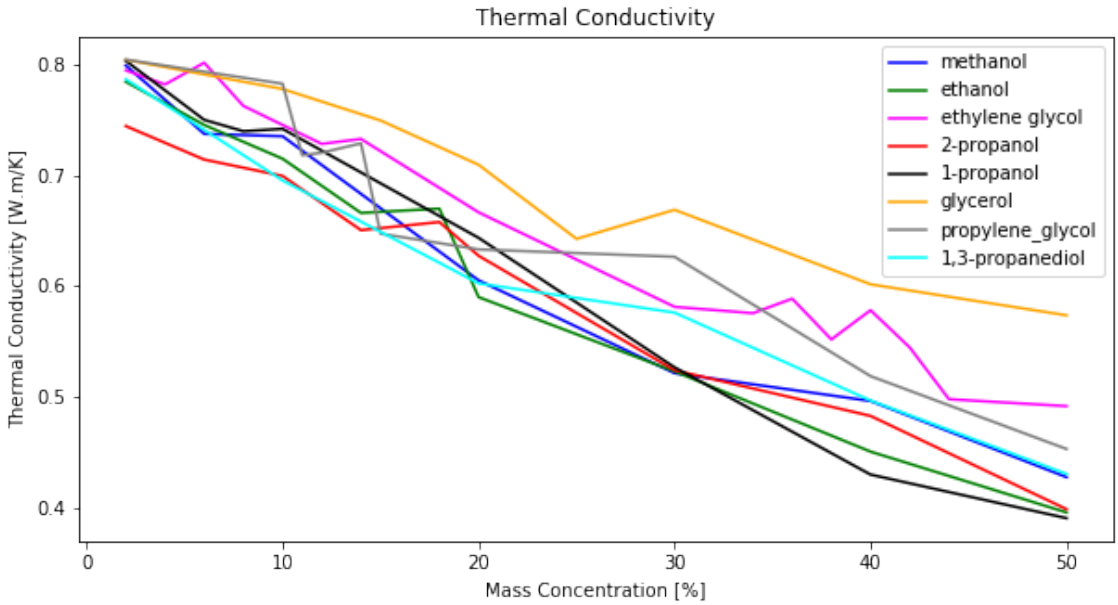


Figure 4.1: Thermal Conductivity Values of 8 Sample Alcohol Types Across Mass Concentration

As expected in the thermal conductivity graph, all the thermal conductivity lines decreased due to the fact that all types of alcohol are less efficient than water in terms of heat transfer. Even though having a decreasing trend, the gradient of the thermal conductivity line of glycerol was quite different compared to others. Due to the absence of enthalpy quantity, all values converge to approximately 0.85 [W/m.K], which is expected.

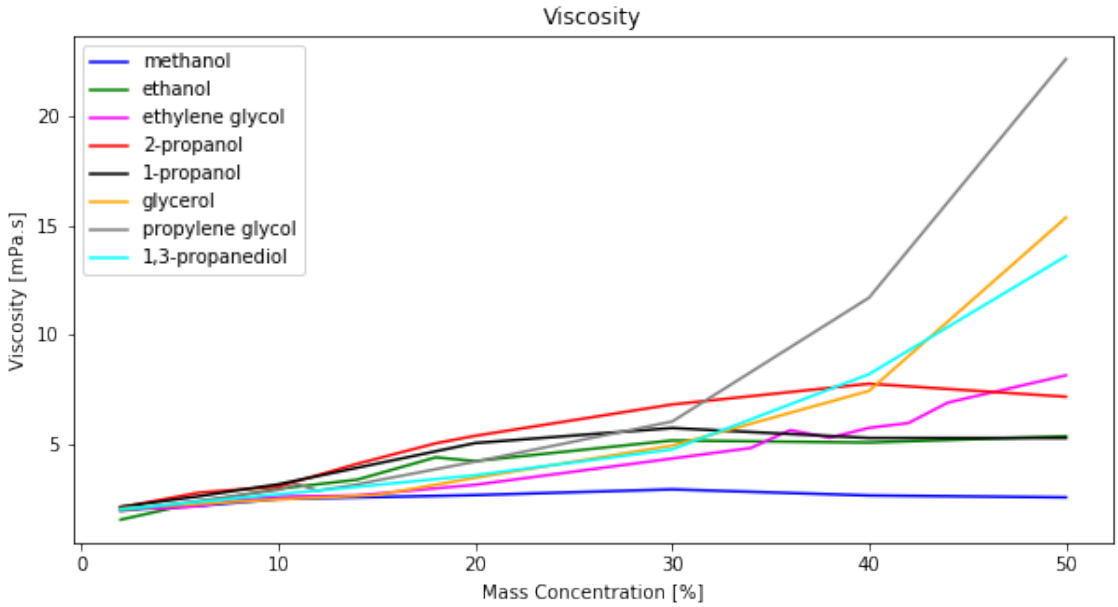


Figure 4.2: Viscosity Values of 8 Sample Alcohol Types Across Mass Concentration

In the viscosity graph, while all values converged to the value of pure water, which is expected, the viscosity line of methanol also decreased as methanol is less viscous than water.

4.2 Model Result Analysis

As mentioned in the method section, the training data will be defined in 5 different ways: randomly divided, excluding all propylene glycol data, excluding all glycerol

data, excluding all methanol data and excluding all 2-propanol data. The result for each data division approach is presented as follows:

Table 4.1: Performance Score on the Testing Data Set

Training Data	TC R^2 Score	Visc R^2 Score
Randomly divided	0.96	0.70
Propylene Glycol data excluded	0.86	0.74
Glycerol data excluded	0.36	0.76
Methanol data excluded	0.92	Failed
2-propanol data excluded	0.90	0.72

The results indicate that for any alcohol that has structural similarities with data in the training set, has a high performance score when used on the testing data set. However, the alcohols that are significantly different from the training sets have a quite low performance scores.

For thermal conductivity models, except for glycerol-excluded approach model, all the models possess a decent performance score. The explanation for this is that the testing sets in such cases are similar to the training sets. While propylene glycol - 1,3-propanediol and 1-propanol - 2-propanol are pairs of structural isomers, methanol is also quite close to ethanol. However, even though the molecular structure of glycerol is not so distinguished to the others, it is the only type of alcohol that had the gradient of the thermal conductivity that trends significantly different from the others; not to mention that glycerol is the only type of alcohol that possesses 3 hydroxyl groups within the molecule. This helps to explain why the glycerol-excluded model performance score is quite low.

A similar explanation can be applied to explain the phenomenon in the viscosity models. In methanol-excluded model, the model failed to predict the viscosity values of methanol. Recalling the simulation data in the previous sub-section, methanol was the only type of alcohol that had a non-increasing value trend. It came from the fact that within the sample, methanol is the only type of alcohol that is less viscous than water. In other words, methanol is very different from the other alcohols when looking from a viscosity point of view. Thus, the model could not predict the viscosity values of methanol since it did not learn any methanol similar relationship during the training process. The other models have moderate performance scores but are not satisfactory. Since these models included methanol in the training process, it is likely that the bizarre viscosity of methanol influenced the prediction ability and resulted in non-satisfactory performance scores.

For future improvement of this method, the sample alcohol types should be diversified to obtain more generalized prediction models. Since low viscosity of methanol is a good point, we should include more alcohol types that are less viscous than water. However, there might be a chance that the selected variables are not sufficient to cover abnormal cases. Thus, independent research on how molecular structures influence the thermophysical properties of unusual alcohol types like methanol should be conducted to improve the variable sets. At the same time, we also need to diversify the sample in terms of structural features. Obviously, the sample alcohol types only have single bonds and straight carbon chain. Thus, the addition of double bonds, triple bonds, circle structures and tree-like carbon chain could help generalize the solutions.

While including methanol in the construction of models can give us a better direc-

tion to prepare data and investigate on a certain direction, I will exclude methanol out of the construction of the model in order to investigate the capability of this methodology for prediction when performance scores are sufficiently high. The expected performance score should be significantly higher than the previous version. Thus, the finalized models performance scores become

Table 4.2: Finalized Models Performance Scores

Thermal Conductivity R^2 Score	Viscosity R^2 Score
0.96	0.91

The models also help us to investigate how variables influence the thermophysical properties using the F-score method (Sasaki, 2007). For the final models, the variable influences (feature importance) are as follows:

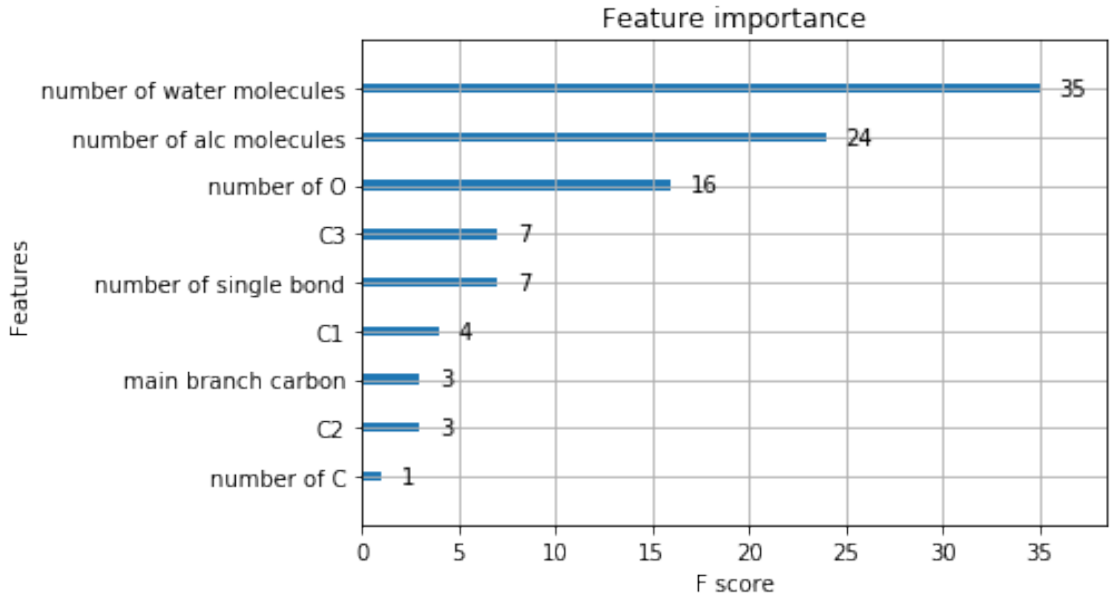


Figure 4.3: Feature Importance of the Thermal Conductivity Model

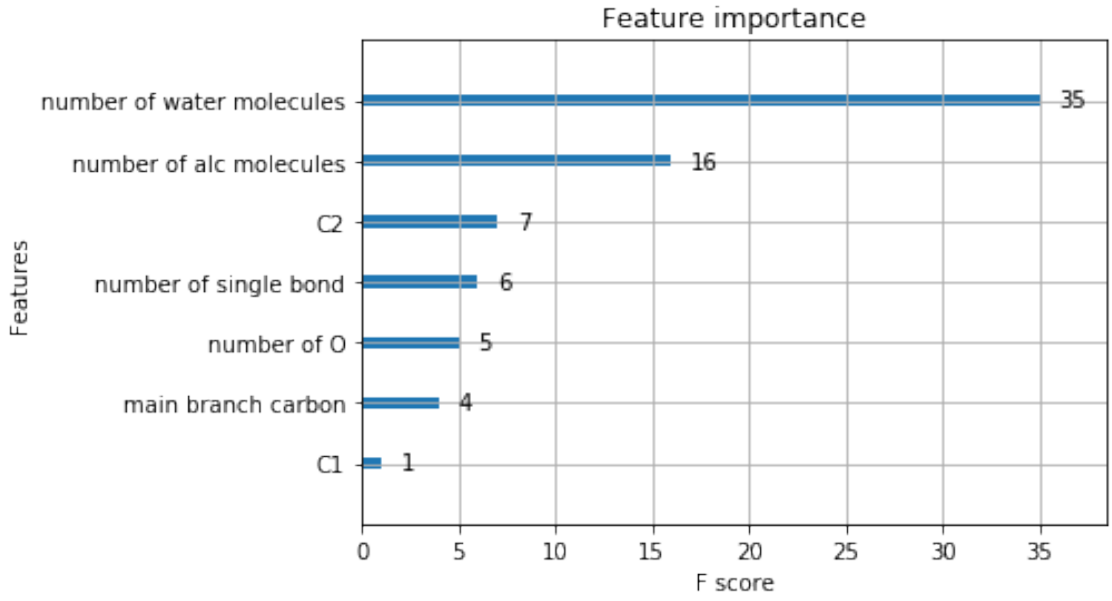


Figure 4.4: Feature Importance of the Viscosity Model

As expected, the mass concentration is one of the main factors that decides the thermal properties of the mixtures by having the number of water molecules and alcohol molecules as the highest influential variables. However, due to some noises and possibly the lack of better variables in the viscosity model, the score of the number of alcohol molecules is slightly underestimated or the score of the number of water molecules is slightly overestimated. Nonetheless the importance of these 2 variables are still clearly shown.

For thermal conductivity, another research (Manjunatha et al., 2017) also showed that the number of hydroxyl groups affect the heat transfer ability of the alcohol. Interestingly, by using machine learning approach, we can also know that the hydroxyl group at the 3rd carbon position in the main carbon chain and the number of single bonds also have a significant influence on the thermal conductivity.

For viscosity, it is the hydroxyl group at the 2nd carbon position in the main carbon chain that significantly affect the viscosity values.

4.3 Optimization Results

Using the formulation 3.4.1 and the related constraints, the results for optimization showed that the alcohol types with the following estimated structural features will have the optimal performance on both thermal conductivity and viscosity:

Table 4.3: Predicted Structural Features From Optimization

Ratio of Molecules (alcohol/water)	Number of carbon	Number of oxygen	Number of single bond	Length of (main) (carbon chain)	Position of hydroxyl groups
0.0005-0.0148	3-4	3	13,17	3	1, 2, 3

Table 4.4: Predicted Thermophysical Properties From Optimization

Predicted Thermal Conductivity (W/m.K)	Predicted Viscosity (mPa.s)
0.81219405	2.0989997

As we can see, the best mixture is almost water, as water so far has the best thermal conductivity and viscosity. Furthermore, one of the molecular structures that can be constructed from these predicted features is glycerol, which is the type of alcohol that has the highest thermal conductivity and quite good viscosity across mass concentrations of alcohol-water mixtures according to the simulated data. This is showing that the methodology is approaching on the right direction. In the future work, with the additional constraint of freezing point, the method will be able to produce the desired outcome. Even though we obtained the features, the

lack of diversity in terms of molecular structure from the sample data prevents us from constructing a complete structure. Thus, in the future where this method is applied, the sample data need to be sufficiently diverse enough as discussed in the previous sub-section. At the same time, an interpreting method should also be developed to translate from the broken down molecular structural features to a complete structure.

Chapter 5

Conclusion

The introduction section showed that there are several obstacles that prevent us from getting a research direction towards the next generation of antifreeze. In this study, I suggested that such problems can be overcome by creating a function that connects the antifreeze structural features to its thermophysical properties such as thermal conductivity and viscosity. The function is created by implementing a supervised machine learning method called xgboost while the data used in training xgboost models is obtained from Green-Kubo relation based molecular dynamics simulations of 8 types of alcohol: methanol, ethanol, ethylene glycol, glycerol, 1-propanol, 2-propanol, 1,3-propanediol and propylene glycol. Such a function helps us to gain clues for constructing the next generation of alcohol coolants while it also shows us a research direction to optimize this method in the future.

Summary of Findings

The training data is decided by 5 different ways: randomly divided, excluding methanol, excluding 2-propanol, excluding glycerol and excluding propylene glycol. The results showed that the models can predict values that have similar patterns to training data, while they had difficulty predicting properties that were very different to the training data. Thus, to overcome this problem in the future, there are 2 different approaches: diversification of the training data and conducting of research on special alcohol types such as methanol.

The machine learning approach can also statistically show that besides factors such as the concentration and number of hydroxyl groups, the hydroxyl group at the 3rd carbon position in the main carbon chain can significantly affect the thermal conductivity values. Similarly, the hydroxyl group at the 2nd carbon position in the main carbon chain has a significant influence on the viscosity values.

For the given alcohol sample excluding methanol, the optimization predicted that the next alcohol antifreeze candidate would possess 3 to 4 carbons, 3 oxygens, 13 or 17 single bonds, a main carbon chain of length 3 and have hydroxyl groups in every position. However, the concentration showed that the mixture is almost water, which makes sense since we are only considering the thermal conductivity and viscosity. Furthermore, one of molecular structures that can be constructed from the predicted structural features is glycerol, the type of alcohol that has the highest thermal conductivity and fairly low viscosity across mass concentration of alcohol-water mixtures according to simulated data. Thus, the results show that the optimization algorithm approaches the problem in an appropriate manner. With the addition of freezing point in the future, the methodology will be able to produce

desired outputs. Furthermore, the prediction is likely to be further improved with a more diverse sample data. An interpreting method is also needed to translate the obtained structural feature values to a complete final structure.

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