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STUDY OF TRANSPORT PROPERTIES OF ASSOCIATING MOLECULAR FLUIDS

Tarun Kumar Dey*

Post Graduate Department of Physics L. S. College, Muzaffarpur-842001.

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***Corresponding Author**
Dr. Tarun Kumar Dey
Post Graduate Department
of Physics L. S. College,
Muzaffarpur-842001.

ABSTRACT

Using the statistical associating fluid theory (SAFT) and decoupled mode theory (DMT) we have developed a generalized model for transport coefficients that reproduces the angular behaviour of the thermal conductivity of pure fluids in the critical region ,unlike the decoupled mode theory model based on the asymptotic cross over equation of state,the statistical associating fluid theory and decoupled mode theory is valid in the entire fluid state region at $T \geq T_e$(T_e is the binomial temperature) and at $\rho \rightarrow 0$ reproduces the dilute gas contribution for the transport coefficients .A comparison is made with experimental data for ethanol and methanol .The agreement is found good.

KEYWORDS: Associating fluid theory ,transport properties , decoupled model theory.

1. INTRODUCTION

The purpose of the present work is to develop a theory to estimate the transport properties like thermal conductivity of associating fluids .In associating fluids such as methanol and ethanol, strong attractive interactions between molecules result in the formation of molecular clusters that have effect on the structural properties of the species. Due to their high polarity and strong self association, are complex fluids that are extremely challenging for both experimental andtheoretical study. Molecular-based equations of state (EOS), such as statistical associating fluid theory (SAFT), employ equations that have been developed as an alternative to empirical EOS for associating liquids .Currently, in combination with the generalized crossover density functional (DFT) and decoupled mode theory (DMT), this procedure has been also extended to the interfacial[1,2] and transport[3] properties of pure fluids.

In this present paper,we have developed a Statistical Associating Fluid Theory (SAFT) and Decoupled Mode Theory (DMT) model for the thermal conductivity of methanol and ethanoland have compared this model with experimental thermal conductivity data.

2. FORMULATION

For the estimation of thermal conductivity of the methanol and ethanol, we apply decoupled-mode theory (DMT) model for the transport coefficients of pure fluids and fluid mixtures developed by Kiselev and Kulikov.[4,5] In the limit of pure components, the crossover expression for the thermal conductivity takes the form[6-7]

$$\lambda = \frac{k_B T \rho C_P}{6\pi \eta_b \hat{\xi}} \Omega(z) + \lambda_b \qquad \textbf{(1)}$$

whereη_b is the viscosity, and λ_b is a background part of the thermal conductivity that can be represented as a sum of the dilute-gas and the residual contributions.

$$\lambda_b(\rho, T) = \lambda^\circ(T) + \Delta\lambda_r(\rho, T) \qquad \textbf{(2)}$$

whereλ° is the dilute-gas thermal conductivity, which depends only on temperature, and $\Delta\lambda_r$ is the residual thermal conductivity. The crossover function $\Omega(z) = \Omega(q_D\xi)$ in eq1 is given by

$$\Omega(z) = \frac{2}{\pi}\left[\tan^{-1}(z) - \frac{1}{\sqrt{1+y_{1D}z}}\tan^{-1}\left(\frac{z}{\sqrt{1+y_{1D}z}}\right)\right] \qquad \textbf{(3)}$$

Where

$$y_{1D} = \frac{6\pi\eta_b^{\,2}}{k_B T \rho q_D(\phi_1 + y_1^{-1})}, \quad y_1 = \frac{k_B T \rho C_P}{6\pi\eta_b \hat{\xi} \lambda_b} \qquad \textbf{(4)}$$

In eqs1-3, q_D is a cutoff wavenumber, the renormalized correlation length is given by[8]

$$\hat{\xi} = \xi_{\mathrm{OZ}} \exp\left(-\frac{1}{q_{\mathrm{D}}\xi_{\mathrm{OZ}}}\right) \qquad \textbf{(5)}$$

where $\xi_{\mathrm{OZ}} = \xi\sqrt{\xi_T/\Gamma_0}$ corresponds to the Ornstein- Zernike approximation for the correlation length[11], and $\phi_1 = \phi(k_{1D}\xi) = \phi(z)$ is the dynamical scaling function[9,10]

$$\phi(z) = \frac{3[1 + z^2 + (z^3 - z^{-1})\tan^{-1}(z)]}{4z^2(1 + z^2)} \qquad \textbf{(6)}$$

Calculated at a constant value of the wavenumber $k_{1D} = 0.1q_D$. Asymptotically close to the critical point at $q_D\xi >> 1$, the parameter $y_1 >> 1$, the crossover function $\Omega(z)$ approaches unity, and the thermal conductivity along .We approximated the dilute-gas contribution for the thermal conductivity of methanol by adopting the correlation[12]

$$\lambda^{(0)}(T) = 5.7992 \times 10^{-7}\, T^{1.7862} \qquad \textbf{(7)}$$

while for ethanol we used the equation recommended by the DIPPR DIADEM program[13]

$$\lambda^{\circ}(T) = \frac{-10.109 \times 10^{-3}\, T^{0.6475}}{1.0 - 7332/T - 268000/T^2} \qquad \textbf{(8)}$$

where the temperature unit is K and the thermal conductivity units are $\mathrm{Wm^{-1}K^{-1}}$. For the residual contribution in both fluids, methanol and ethanol, we use here a polynomial in temperature and density

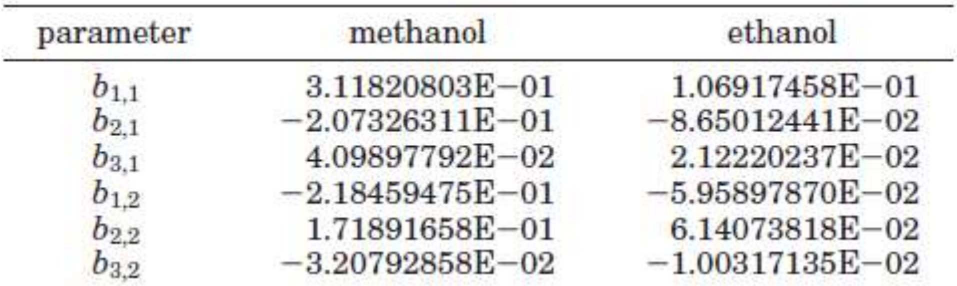
$$\Delta\lambda_{\mathrm{r}}(\rho, T) = \sum_{i=1}^{3}\left(b_{i,1} + b_{i,2}\frac{T}{T_{\mathrm{c}}}\right)\left(\frac{\rho}{\rho_{\mathrm{c}}}\right)^{i} \qquad \textbf{(9)}$$

which has recently been shown to accurately represent hydrocarbon fluids such as isobutane,[14] butane,[15] and propane.[16] The parameters $b_{i,j}$(i = 1-3, j = 1, 2) in the residual contribution have been found from a fit of the GC SAFT-DMT model to the selected data sets for methanol[17,18,19] and ethanol[19,20,21] that cover a wide range of temperature and pressure conditions above and below the critical point.

3. RESULTS AND DISCUSSION

The values of the coefficients $b_{i,j}$in eq8 for methanol and ethanol are listed in Table 1, and comparisons with the experimental thermal conductivity data are shown in Figures 1-3. For both substances, very good agreement between the GC SAFTDMT model and experimental thermal conductivity data is observed. The GC SAFT-DMT model reproduces all thermal conductivity data for methanol (*n* = 430) and ethanol (*n*= 230) with an AAD of 0.85%. The sharp maxima of the thermal conductivity observed at *P*) 10 MPa and *T*) 512 K in methanol (Figure 1) and at near critical pressures at *T*) 520 K for ethanol (Figure 3) correspond to the critical enhancements caused by long-range density fluctuations as described by the first term in right-hand side of eq1

Table 1: Coefficients $b_{i,j}$ in equation 8 for Thermal Conductivity of Methanol and Ethanol.



parameter	methanol	ethanol
$b_{1,1}$	3.11820803E−01	1.06917458E−01
$b_{2,1}$	−2.07326311E−01	−8.65012441E−02
$b_{3,1}$	4.09897792E−02	2.12220237E−02
$b_{1,2}$	−2.18459475E−01	−5.95897870E−02
$b_{2,2}$	1.71891658E−01	6.14073818E−02
$b_{3,2}$	−3.20792858E−02	−1.00317135E−02

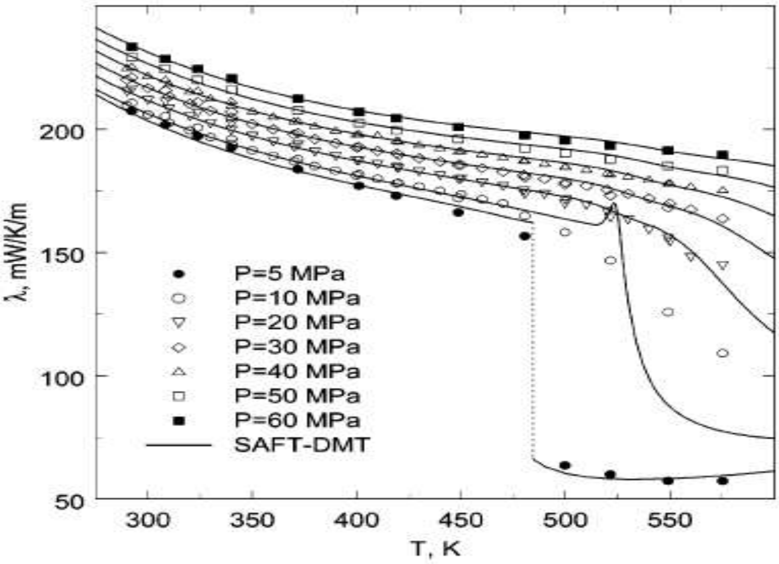


Figure 1: Thermal conductivity data for methanol [19, 20] (symbols) with predictions of the SAFT-DMT model (curves).

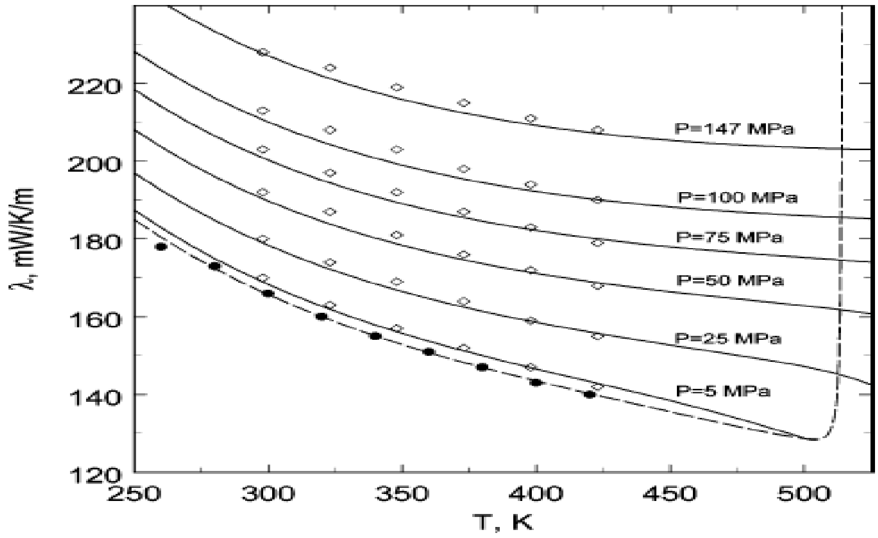


Figure 2: Thermal conductivity data for ethanol along isobars[15] (empty symbols) and along the saturated curve[18] (filled symbols) as a function of temperature with predictions of the SAFT -DMT model (curves).

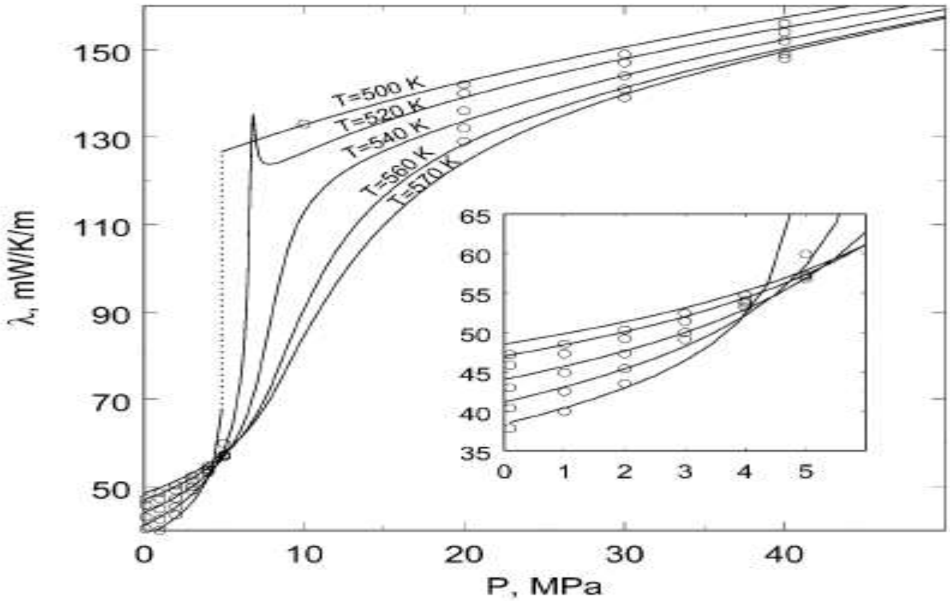


Figure 3: Thermal conductivity data for ethanol along isotherms[19] (symbols) as a function of pressure with predictions of the SAFT-DMT model (curves).

can see, the maxima of the thermal conductivity, observed at $\rho \cong \rho_c$, increase drastically as the pressure and temperature approach their critical values.

4. CONCLUDING REMARKS

In this work, we have developed a GC SAFT EOS model for *n*-alkanols by incorporating the crossover approach developed by Kiselev into the analytical SAFT equation for associating fluids developed by Huang and Radoz,[21-22] model.Further this model is appliedfor transport properties.This model has been tested against experimental thermal conductivity for methanol and ethanol.The next step is applying this model to mixture prediction and computation. Work in this direction is now in progress, and the results will be reported in future publications.

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