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Cubic Equations of State for Transport Properties: An Equation for the Thermal Conductivity of Oxygen

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A scheme for the development of equations for the transport properties in terms of pressure and temperature, so-called transport equations of state, is presented. The surfaces of transport properties and density as a function of pressure and temperature reveal similarities, which become even more evident when the residual transport property as a function of pressure and temperature is considered. Even the spinodals of transport and thermal properties coincide in the p, T plane, as can be shown mathematically and as was already empirically found for water and oxygen. Based on these similarities a cubic transport equation of state is evaluated for the residual thermal conductivity of oxygen. The new equation is only a little less accurate than the already established virial transport equation of state for oxygen. It is, however, much simpler and needs only a few parameters. The accuracy is still good enough for practical applications. The results demonstrate that cubic equations of state can describe transport properties and are a basis for generalized estimation methods for the transport properties of fluids.

KEY WORDS: equation of state (cubic); oxygen; thermal conductivity; transport equation of state.

1. INTRODUCTION

Only a few attempts have been made to describe the transport properties thermal conductivity and viscosity in terms of pressure and temperature over the entire fluid range by means of a single consistent equation for both phases. The kinetic and molecular theories describe transport properties as functions of density and temperature and therefore most of the correlations of transport properties contain density and temperature as independent

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variables. A thermal equation of state is needed, then, to determine the density. Errors in the density affect the accuracy of the transport property. It is therefore of some practical interest to calculate transport properties as a function of temperature and pressure.

Previous studies [1–4] revealed that equations of the form

$$p = F(\mathrm{TP}, T) \tag{1}$$

with pressure p, temperature T, and transport property TP best represent the surfaces of the transport properties. Based on apparent similarities between the surfaces of transport properties and the density, a so-called transport equation of state of the virial type has already been established for water [1], oxygen [2, 3], and nitrogen [4]. This transport equation of state contains 21 adjustable coefficients and describes the transport properties within their experimental accuracy. A complete data set covering the entire fluid range is necessary to fit the coefficients of the equation properly. The basic structure of the transport equation of state is similar to that of the thermal equation of state developed by Bender [5].

When experimental data over the entire fluid range do not exist, cubic equations of state seem to be more suitable because they have proven successful in predicting thermodynamic properties, expecially at higher pressures. Moreover, generalized cubic equations of state can predict thermodynamic properties when experimental data are lacking.

Cubic equations of state, however, have not yet been applied to the transport properties of fluids. In the following such an equation shall be derived in order to evaluate how accurately transport properties can be represented. The thermal conductivity of oxygen is chosen as an example, because an accurate virial transport equation of state is already available [3] for comparison.

2. BACKGROUND

For the development of transport equations of state in terms of pressure and temperature, a general scheme can be established when the following assumptions are made.

(1) The transport properties of fluids are variables of state. As a consequence the transport property of a pure substance is determined by two variables of state, e.g., pressure and temperature or density and temperature. Non-Newtonian and anisotropic fluids are not considered.

(2) An anomalous behavior of the transport properties around the critical point is not considered. According to Sengers [6] one

can separate the thermal conductivity into a background contribution and an additive singular contribution, which accounts for the critical enhancement. In this paper only the background contribution is dealt with.

(3) The isotherms of the transport properties are strictly monotonic increasing functions of the density.

(4) An equation for the transport properties should be explicit in pressure, because otherwise the functional form is not univalent and singularities at the critical point occur [1–4].

The transport property at constant temperature is only a function of density ρ

$$\mathrm{TP} = f(\rho) \tag{2}$$

Because of the third assumption the inverse function can be formed and is univalent,

$$\rho = f^{-1}(\mathrm{TP}) \tag{3}$$

The thermal equation of state for an isotherm reads

$$p = \varphi(\rho) \tag{4}$$

Replacing the density one obtains the transport equation of state for an isotherm

$$p = \varphi[f^{-1}(\mathrm{TP})] \tag{5}$$

For all isotherms one obtains the transport equation of state, Eq. (1):

$$p = F(\mathrm{TP}, T)$$

Previous transport equations of state [1–4] were based on an analysis of the surfaces of transport properties. The isotherms in a p, ρ diagram (Fig. 1) are very similar to the isotherms in a p, TP diagram (Fig. 2). In order to describe the transport properties by means of pressure-explicit equations, a fold-like shape for the subcritical isotherms of the transport properties inside the two-phase region was assumed [1, 3], as is known for the isotherms of the density. Furthermore, accurate experimental data of the transport properties of water and oxygen reveal that the spinodals of the transport properties coincide with the spinodals of the density in the p, T plane [1, 3]. In other words, the p, T coordinates of points G and L in Figs. 1 and 2 for each subcritical isotherm are the same.

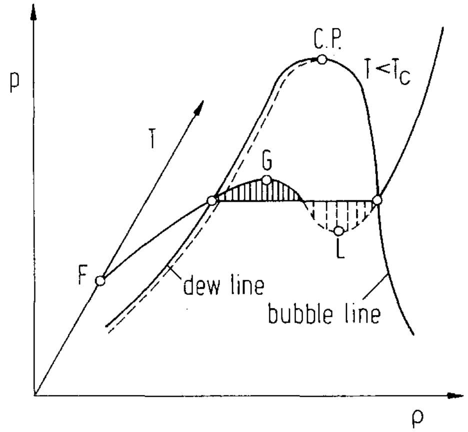


Fig. 1. Subcritical isotherm of the density. Critical point: C. P. Points of the spinodal: *G*, *L*.

In the following it will be shown that the assumption of a fold is reasonable and that the spinodals of both transport and thermal properties coincide in the p, T plane.

The spinodal of the thermal properties is defined by

$$\left[\frac{\partial p}{\partial \rho}\right]_T = 0 \tag{6}$$

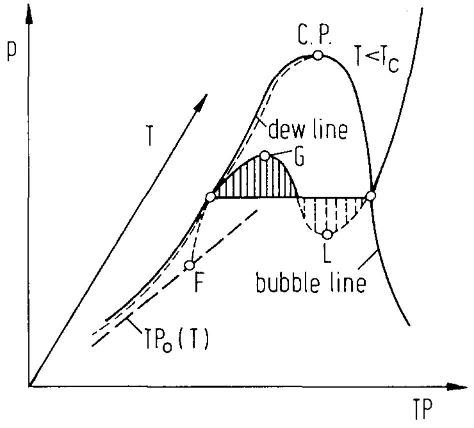


Fig. 2. Subcritical isotherm of the transport property. Critical point: C. P. Points of the spinodal: *G*, *L*; dilute gas: ------.

For a given temperature T the points of the spinodal are obtained from Eq. (6) and the thermal equation of state, Eq. (4). The maximum on the gas branch of the isotherm, point G in Fig. 1, is characterized by

$$\left[\frac{\partial^2 p}{\partial \rho^2}\right]_T < 0 \tag{7}$$

The ordinate of the maximum shall be p_G.

The minimum on the liquid branch, point L in Fig. 1, with the ordinate p_L is characterized by

$$\left[\frac{\partial^2 p}{\partial \rho^2}\right]_T > 0 \tag{8}$$

At the critical point both extremes fall together in one point with an inflectional horizontal tangent:

$$\left[\frac{\partial^2 p}{\partial \rho^2}\right]_T = 0 \tag{9}$$

In order to analyze the behavior of a subcritical isotherm of the transport properties at the points of the spinodal, the partial differential of the pressure over the transport property at constant temperature T is written as

$$\left[\frac{\partial p}{\partial \mathrm{TP}}\right]_T = \left[\frac{\partial p}{\partial \rho}\right]_T \left[\frac{\partial \rho}{\partial \mathrm{TP}}\right]_T \tag{10}$$

From Eq. (10) it is evident that $(\partial p/\partial \mathrm{TP})_T$ becomes zero if and only if $(\partial p/\partial \rho)_T$ equals zero, Eq. (6), because the term $(\partial \rho/\partial \mathrm{TP})_T$ is positive and finite. For a given temperature T, Eq. (6) is satisfied at the points where the pressure coordinates are p_G and p_L. Therefore the isotherm with temperature T of the transport property exhibits points with horizontal tangents at the same pressure values. The kind of extremes, minima or maxima, remains the same as is shown by means of the second partial differential of the pressure over the transport property for the points of the spinodal:

$$\left.\frac{\partial^2 p}{\partial \mathrm{TP}^2}\right|_{T,\mathrm{Sp}} = \left[\frac{\partial^2 p}{\partial \rho^2}\right]_{T,\mathrm{Sp}} \left[\frac{\partial \rho}{\partial \mathrm{TP}}\right]_{T,\mathrm{Sp}} \tag{11}$$

The sign on the right-hand side of Eq. (11) is determined by the term $(\partial^2 p/\partial \rho^2)_{T,\mathrm{Sp}}$ and therefore determined by Eqs. (7) and (8). In the case of the critical point, a point with an inflectional tangent is obtained according to Eq. (9), as previously derived [7].

When a maximum and a minimum of the subcritical isotherms of the transport properties inside the two-phase region exist, it is clear that a fold-like shape of the isotherms in this region is a reasonable assumption. For a given temperature the extremes appear at the same pressures as those of the isotherms of the density. Therefore, the projection of the spinodal of both transport and thermal properties yields identical curves in the p, T-plane.

In spite of the similarities of the isotherms of both properties in Figs. 1 and 2, a principal difference is obvious. Due to the temperature dependence of the transport properties of the ideal gas, $\mathrm{TP}_0(T)$, the gas branch of the isotherm of the transport property lies on the right-hand side of the dew line when projected into the p, TP plane in Fig. 2. In other words, the transport property of a saturated vapor is smaller than the transport property at the same pressure and higher temperature.

Subtracting the ideal gas value TP_0 from the transport property TP, the residual transport property $\Delta\mathrm{TP}$ is obtained. The shape of the isotherm in a p, $\Delta\mathrm{TP}$ representation, Fig. 3, corresponds much better to that of the density (see Fig. 1).

The residual transport property $\Delta\mathrm{TP}$ is defined by

$$\Delta\mathrm{TP} = \mathrm{TP} - \mathrm{TP}_0 \tag{12}$$

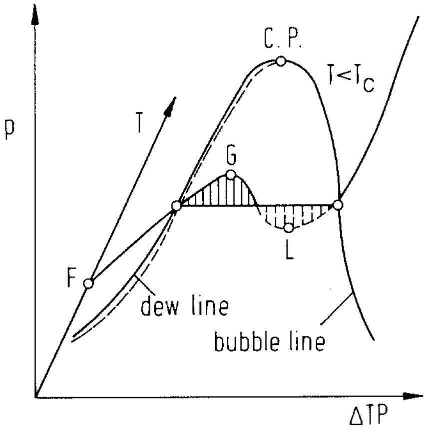


Fig. 3. Subcritical isotherm of the residual transport property. Critical point: C. P. Points of the spinodal: G, L.

As is well known, it does not depend or depends only slightly, on the temperature [8, 9]. The transport property in Eqs. (1), (2), (3), and (5) can therefore be replaced by its residual property.

3. CORRELATIONS

The scheme will now be applied to the thermal conductivity of oxygen with the aim to develop an accurate equation with as few parameters as possible.

All properties are reduced by their values at the critical point

$$p_\mathrm{r} = p/p_\mathrm{c} \tag{13}$$

$$T_\mathrm{r} = T/T_\mathrm{c} \tag{14}$$

$$\rho_\mathrm{r} = \rho/\rho_\mathrm{c} \tag{15}$$

except the residual thermal conductivity which is reduced by

$$\Delta\lambda_\mathrm{r} = \Delta\lambda/\Lambda \tag{16}$$

with

$$\Lambda = \frac{\mathscr{R}^{5/6} p_\mathrm{c}^{2/3}}{T_\mathrm{c}^{1/6} M^{1/2} N_\mathrm{A}^{1/3}} \tag{17}$$

according to a dimensional analysis [10]. Here $\mathscr{R}$ is the universal gas constant, M is the molar mass and N_A the Avogadro constant.

The characteristic constants of oxygen are [3]

$$p_\mathrm{c} = 5.0433\ \mathrm{MPa}, \qquad T_\mathrm{c} = 154.581\ \mathrm{K}$$

$$\rho_\mathrm{c} = 436.14\ \mathrm{kg \cdot m^{-3}}, \qquad M = 31.999\ \mathrm{kg \cdot kmol^{-1}}$$

The inverse function $\rho_r(\Delta\lambda_r)$ of the thermal conductivity of oxygen is shown in Fig. 4. The different isotherms form a single curve, which is well represented by the empirical equation

$$\rho_\mathrm{r} = \frac{1}{v_\mathrm{r}} = \frac{\Delta\lambda_\mathrm{r}}{a + b\Delta\lambda_\mathrm{r}^{0.8}} \tag{18}$$

where the parameters a and b were fitted to recommended residual thermal conductivities of oxygen as a function of density from [3].

An empirical equation was adopted, because up to now no theoretically based equation for the residual transport property exists.

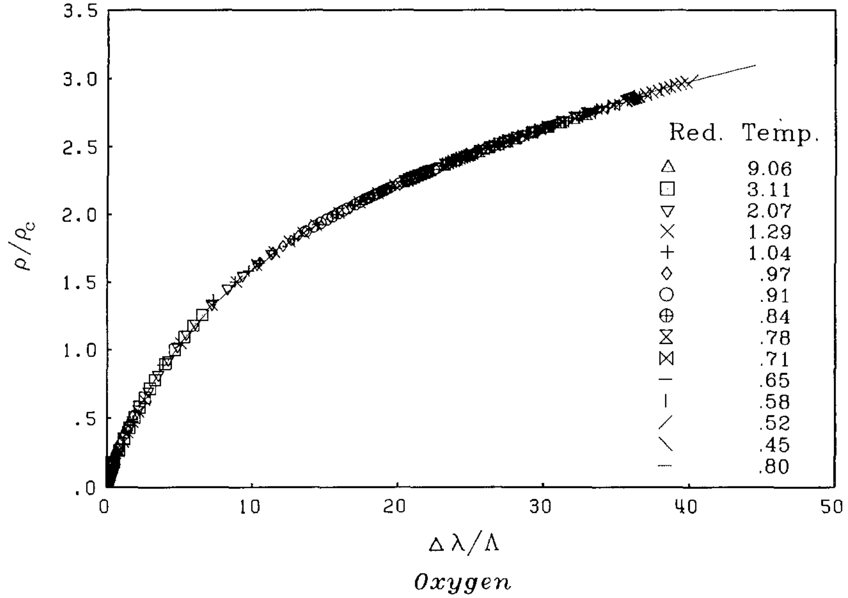


Fig. 4. Inverse function $\rho(\Delta \mathrm{TP})$ for the thermal conductivity of oxygen. Symbols, recommended values [3]; line, calculated by means of Eq. (18).

The thermal properties are represented by a cubic equation of state with three temperature-dependent parameters:

$$p_r = \frac{Z_c T_r}{v_r} - \frac{A}{(v_r + B)\, v_r} + \frac{C}{(v_r + B)\, v_r^2} \tag{19}$$

where

$$A = A_1 T_r + A_2 \tag{20}$$

$$B = B_1 T_r^2 + B_2 T_r + B_3 \tag{21}$$

$$C = C_1 T_r^2 + C_2 T_r + C_3 \tag{22}$$

Z_c represents the critical compressibility.

Equation (19) was derived from a general generating cubic equation of state proposed by Martin [11]. It represents the density of oxygen with an absolute average deviation of 0.6%. Maximum deviations of about 10% occur in the critical region. However, an accurate description of the critical region is beyond the scope of this paper.

For the determination of the parameters in Eqs. (18) and (19) recommended values of the thermal conductivity of oxygen from Laesecke [3] were used. These recommended values were evaluated by means of a critical comparison of experimental data from different literature sources. The data of Keyes [12], Ivanova et al. [13], and Roder [14] were finally correlated and tables of the thermal conductivity of oxygen were generated covering a temperature range 70–1400 K and a pressure range from 0.1 up to 100 MPa. Their estimated accuracy varies from 3% at atmospheric pressure to 18% near the critical point [3]. Subtracting the thermal conductivity of the dilute gas from the tabulated values, recommended residual thermal conductivities as a function of pressure and temperature are obtained. The parameters of both Eqs. (18) and (19) were fitted simultaneously to a total of 733 recommended values of the residual thermal conductivity of oxygen and yielded

$$\begin{array}{llll} a = 2.92364 & A_1 = -2.557545 & B_1 = 0.01788827 & C_1 = -0.01904237 \\ b = 0.5132937 & A_2 = 5.615214 & B_2 = -0.01277994 & C_2 = -0.2257398 \\ & & B_3 = -0.2658302 & C_3 = 1.5613221 \end{array}$$

with a mean relative error in the residual thermal conductivity of −0.24%, a standard deviation of 8.5%, and an absolute average deviation of 3.42%.

Figure 5 shows the reduced pressure versus reduced residual thermal

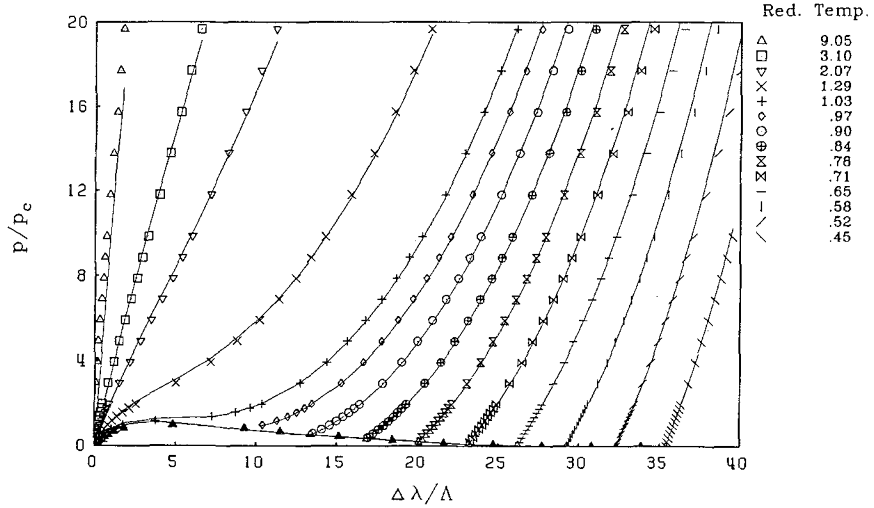


Fig. 5. Reduced pressure versus reduced residual thermal conductivity of oxygen for different reduced temperatures. Symbols, recommended values [3]; lines, calculated by means of Eqs. (18) and (19); saturation, ▲.

conductivity for different temperatures. The recommended data are marked with symbols whereas the calculation is represented by the solid line. Except for the region around the critical point, the new equation represents the recommended values satisfactorily.

The departure plots, Figs. 6a and b, reveal good agreement for

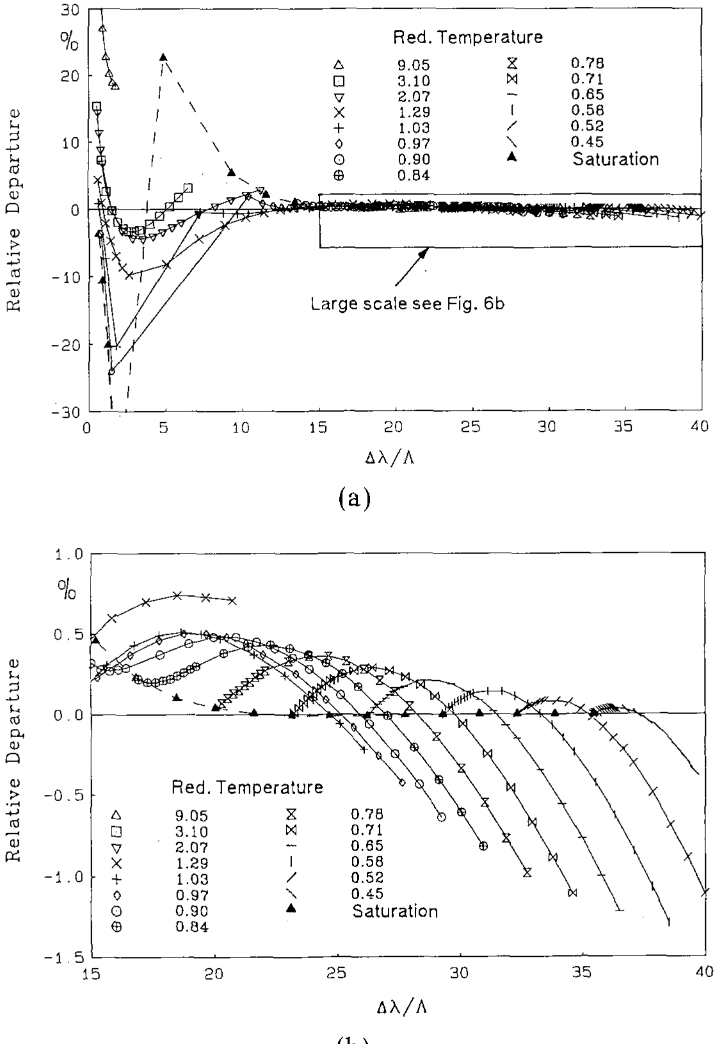
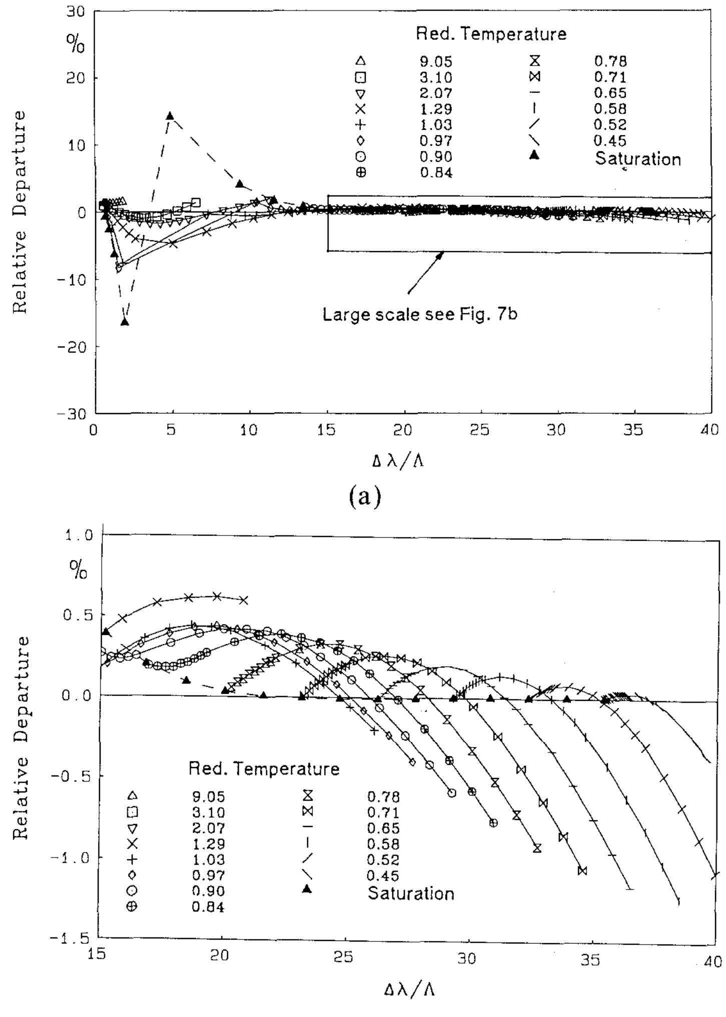


Fig. 6. (a) Departures of the cubic transport equation of state from recommended data [3] for the residual thermal conductivity of oxygen versus reduced residual thermal conductivity. (b) Departures at high residual thermal conductivities.

reduced residual thermal conductivities above values of 10. For lower residual thermal conductivities, the errors increase because then the residual thermal conductivities become small compared with the thermal conductivity of the dilute gas.

The property of interest is, of course, the thermal conductivity itself rather than its residual part. Therefore departure plots for the thermal



(a)

(b)

Fig. 7. (a) Departures of the cubic transport equation of state from recommended data [3] for the thermal conductivity of oxygen versus reduced residual thermal conductivity. (b) Departures at high residual thermal conductivities.

conductivity are shown in Figs. 7a and b. They clearly demonstrate that the errors reduce drastically at low residual thermal conductivities. The mean relative error for the thermal conductivity is −0.4% with a standard deviation of 3.6%. The absolute average deviation is 0.9%.

The virial transport equation of state for oxygen [3] yielded a mean relative error in the thermal conductivity less than 0.01% with a standard deviation of 0.7% and an absolute average deviation of 0.5%. It is more accurate than the new equation. However, the difference in accuracy between the two is about the same as that for virial and cubic thermal equations of state. The cubic transport equation of state has a relatively simple structure and is therefore easier to solve numerically than the more complex virial transport equation of state.

4. CONCLUSIONS

Phenomenological investigations reveal that the previously stated similarities [1–4] between the surface of transport properties and the density become more pronounced when only the residual part of the transport property is considered. Also, the spinodals of transport and thermal properties coincide in the p, T plane, as already known from empirical studies [1, 3]. In a similar way as for the thermal properties, cubic equations of state can describe the transport properties as a function of pressure and temperature. Also, the residual transport properties can be represented in terms of pressure and temperature, which is demonstrated for the thermal conductivity of oxygen. Since generalized cubic equations of state are known to permit predictions of thermodynamic properties, they also seem to be a basis for generalized estimation methods for the transport properties of fluids in terms of pressure and temperature.

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