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Prediction of Transport Properties of Dense Gases and Liquids by the Peng–Robinson (PR) Equation of State[1]

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An attempt is made in this work to combine the Enskog theory of transport properties with the simple cubic Peng–Robinson (PR) equation of state. The PR equation of state provides the density dependence of the equilibrium radial distribution function. A slight empirical modification of the Enskog equation is proposed to improve the accuracy of correlation of thermal conductivity and viscosity coefficient for dense gases and liquids. Extensive comparisons with experimental data of pure fluids are made for a wide range of fluid states with temperatures from 90 to 500 K and pressures from 1 to 740 atm. The total average absolute deviations are 2.67% and 2.02% for viscosity and thermal conductivity predictions, respectively. The proposed procedure for predicting viscosity and thermal conductivity is simple and straightforward. It requires only critical parameters and acentric factors for the fluids.

KEY WORDS: Enskog theory; equation of state; fluids (dense); thermal conductivity; viscosity.

1. INTRODUCTION

The properties of a fluid can be divided into two kinds, equilibrium properties and transport properties. The predictions of equilibrium properties of fluids have been made great progress in recent years. More and more

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equations of state are appearing in the literature. The equation of state can be used accurately to predict the equilibrium properties, such as density, enthalpy, vapor pressure, fugacity and fugacity coefficient, vapor liquid equilibrium, and all kinds of excess properties. Furthermore, the application of equations of state is not only accurate but very convenient. The simplest equation of state of a real fluid is in the form of cubic in volume. Another important advantage of using an equation of state is that it can provide a unique and consistent model for all equilibrium properties. One of the most popular cubic equations of state is that proposed by Peng and Robinson (PR) [1] a dozen years ago. The PR equation is widely used in chemical engineering process simulation, design, and optimization.

On the other hand, transport properties are also important quantities required in engineering design for production, fluid transportation, and processing. There are a lot of articles about the correlation of viscosity and conductivity. However, our understanding of the transport properties is far behind that of equilibrium properties. There is no satisfactory theory of transport properties of real dense gases and liquids. The difficulties we face in the study of transport properties are twofold: one is the inherent difficulties involved in accurate measurements, and the other is the complexity involved in theoretical treatments. Therefore, the generally used correlations of transport coefficient are either empirical or based on some theoretical foundation. A priori, one would expect a theoretically based correlation to be more satisfactory in that better accuracy may be obtained and fewer difficulties might be encountered with extrapolations outside the range of correlation.

Enskog [2, 3] developed a popular theory for the transport properties of dense gas based on the distribution function. However, the Enskog theory was proposed for rigid spherical molecules. For real gases, some modification is needed. Following the Enskog theory, many correlations have been proposed in the form of the reduced density and reduced temperature. A compilation of such correlations can be found in the book of Reid et al. [4]. Among those, Sengers [5] examined the Enskog theory with an emphasis on the behavior of transport properties in the critical region. Cohen and Sandler [6] developed an empirical correlation for density and temperature dependence. Hanley et al. [7, 8] and DiPippo et al. [9] also developed similar correlations. Most of these works have the emphasis on the relation between density and pressure at fixed temperature. The equations of state provide a good description of density, pressure, and temperature. We try to combine the Enskog theory with the popular simple cubic equation of state in this work. The modification is made only on the coefficient of Enskog equations of thermal conductivity and viscosity coefficient.

2. THEORY

Many calculations of the transport coefficients at elevated densities are based on the theory of Enskog [2] for a dense gas of rigid spherical molecules. According to the theory of Enskog the viscosity coefficient η and the thermal conductivity λ for a gas of rigid spheres are represented by the following expressions:

$$\eta = \eta_0 b\rho [1/b\rho\chi + 0.800 + 0.7614(b\rho\chi)^2] \tag{1}$$

and

$$\lambda = \lambda_0 b\rho [1/b\rho\chi + 1.200 + 0.755(b\rho\chi)^2] \tag{2}$$

where η_0 and λ_0 are the dilute-gas viscosity coefficient and thermal conductivity, ρ is the molecular density, $b = 2\pi\sigma^3/3$ is the covolume, where σ is the molecular diameter, and χ is the value of the equilibrium radial distribution function at a distance σ from the center of an individual molecule, for which a number of coefficients in its virial expansion are known:

$$\chi = 1. + 0.6250 b\rho + 0.2869(b\rho)^2 + 0.115(b\rho)^3 + 0.109(b\rho)^4 + \cdots \tag{3}$$

However, the interaction between the real molecules is not of a rigid-sphere nature. Equations (1) and (2) cannot be used directly for real gases. Enskog [2] suggested that Eqs. (1) and (2) can be used to represent the transport coefficients of a real gas over a large density range by attributing effective values to the parameters b and χ deduced from the compressibility isotherms of the substance. In this way one can also partially account for the influence of attractive forces between the molecules. Enskog suggested that $b\rho\chi$ should be determined from compressibility experiments, using the "thermal pressure":

$$b\rho\chi = \frac{1}{R}\left(\frac{\partial V P}{\partial T}\right)_v - 1 \tag{4}$$

where R is the gas constant. P, V, and T are the pressure, volume, and temperature, respectively. In order that the modified Boltzmann equation introduced by Enskog reduces to the ordinary Boltzmann equation at low densities, one should still require

$$\lim_{\rho \to 0} \chi = 1 \tag{5}$$

Many correlations have been suggested in the literature [6] for $b\rho\chi$. However, we try another approach here with the equation of state directly incorporated into Eqs. (1) and (2).

The Peng–Robinson [1] (PR) equation of state is simple in cubic form of volume as:

$$P = \frac{RT}{V-b'} - \frac{a(T)}{V(V+b')+b'(V-b')} \tag{6}$$

where $a(T)$ is the attractive parameter, expressed as a function of temperature, the critical parameters, and the acentric factor of substance.

$$a(T) = a(T_c)\,\alpha(T) \tag{7}$$

$$a(T_c) = 0.45724\frac{R^2T^2}{P_c} \tag{8}$$

$$\alpha(T) = [1 + m(1 - T_r^{0.5})]^2 \tag{9}$$

$$m = 0.37464 + 1.54226\omega - 0.26997\omega^2 \tag{10}$$

where T_c, P_c, and ω are the critical temperature, critical pressure, and acentric factor, respectively. The reduced temperature is defined as $T_r = T/T_c$.

b' is also correlated with the critical parameters and treated as temperature independent.

$$b' = 0.07780\frac{RT_c}{P_c} \tag{11}$$

Substituting Eq. (6) into Eq. (4) the following equation can be obtained:

$$b\rho\chi = \frac{V}{R}\left[\frac{R}{V-b'} + \frac{a(T_c)[m+m^2(1-T_r^{0.5})]}{V(V+b')+b'(V-b')}\frac{1}{(TT_c)^{0.5}}\right] \tag{12}$$

With the limitation of Eq. (5)

$$\begin{aligned} b &= \lim_{\rho\to 0} b\chi \\ &= \lim_{\rho\to 0}\left[\frac{V^2}{V-b'} - V + \frac{a(T_c)[m+m^2(1-\sqrt{T_r})]}{R\sqrt{TT_c}}\frac{V^2}{V(V+b')+b'(V-b')}\right] \\ &= b' + \frac{a(T_c)[m+m^2(1-\sqrt{T_r})]}{R\sqrt{TT_c}} \end{aligned} \tag{13}$$

So the following equation can be obtained:

$$b\rho = \frac{1}{V}\left(b' + \frac{a(T_c)[m+m^2(1-\sqrt{T_r})]}{R\sqrt{TT_C}}\right) \tag{14}$$

With Eqs. (12) and (14), Eqs. (1) and (2) can be calculated directly. This procedure was carried out for the simple fluids. Comparison of the behavior thus predicted with the experimental data is presented in Figs. 1 and 2 for methane. The dashed curves represent the predictions of the above procedure. It is seen that the predicted values are systematically higher than the values of experimental data. The Enskog theory is developed for rigid-sphere molecules. Some modifications must be introduced to improve the accuracy of the correlation for real fluids. It is found empirically that only a substance-dependent constant is required. Equation (1) is modified as

$$\eta = \eta_0(b\rho)\left[\frac{1.000}{(b\rho\chi)} + A + 0.7614(b\rho\chi)\right] \tag{15}$$

where A is a substance-dependent parameter and independent of temperature and pressure. The calculated results with this modification are also shown in Fig. 1 (solid curve).

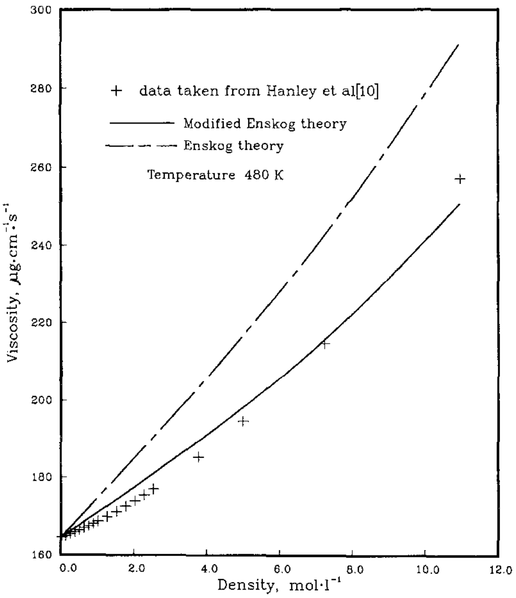

Fig. 1. Density dependence of viscosity of methane. Comparison of the calculated results using the Enskog theory and modified Enskog theory (developed in this work) with the literature data. Data taken from Hanley et al. [10].

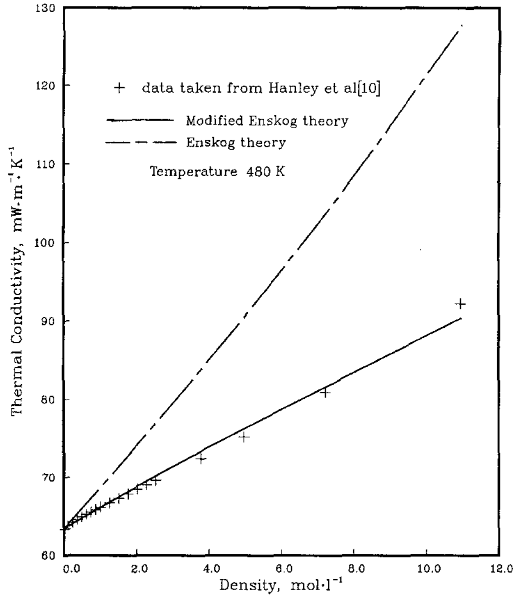

Fig. 2. Density dependence of thermal conductivity of methane. Comparison of calculated results using the Enskog theory and modified Enskog theory (developed in this work) with the literature data. Data taken from Hanley et al. [10].

The Enskog theory describes the density dependence only of the thermal conductivity resulting from the translational degree of freedom. Dymond [15] studied this problem recently for methane. The internal degrees of freedom of the molecules must be taken into account, for its contribution will vary much less with increasing density. The thermal conductivity can be written as the summation of two parts:

$$\lambda = \lambda^{\mathrm{tr}} + \lambda^{\mathrm{int}} \tag{16}$$

where

$$\lambda^{\mathrm{tr}} = \lambda_0[1.00 + 1.200(b\rho\chi) + 0.755(b\rho\chi)^2] \tag{17}$$

represents the contribution of the translational degrees of freedom only and

$$\lambda^{\mathrm{int}} = \lambda_0 - \frac{15}{4} k\eta_0 \tag{18}$$

where λ^{tr} and λ^{int} are the translational and internal contributions to the total thermal conductivity and k is the Boltzmann constant. Combining Eqs. (17), (18), and (16) gives

$$\lambda = \lambda_0 \left[1.00 + \frac{1.200(b\rho\chi)}{D} + \frac{0.755(b\rho\chi)^2}{D} \right] \tag{19}$$

where $D = 4\lambda_0/15k\eta_0$, and for monatomic molecules,

$$\frac{\lambda_0}{\eta_0} = 2.5 \frac{C_v}{M} \tag{20}$$

where M is molecular weight and C_v is heat capacity and a function of temperature.

3. CALCULATED RESULTS

Equations (15) and (19) are the basis of the present calculation where $b\rho$ and $b\rho\chi$ are calculated through Eqs. (12) and (14). The critical temperature, critical pressure, and acentric factor of the substance are required

Table I. Comparisons of Calculated Results for Argon[a]

No.	T (K)	NDP	P, range (atm)	λ AAD %	η AAD %
1	90	18	1-98	1.17	
2	100	18	1–296	2.21	
3	110	18	1–296	3.05	
4	130	18	1–296	3.62	
5	220	15	1–296	5.39	4.08
6	250	15	1–296	4.00	3.01
7	280	16	1–493	3.13	3.03
8	300	17	1–740	3.29	3.17
9	330	17	1–740	2.38	2.49
10	380	17	1–740	1.84	2.41
11	400	17	1–740	1.63	1.90
12	430	17	1–740	1.38	1.86
13	450	17	1–740	1.08	1.84
14	480	17	1–740	0.80	1.80
15	500	17	1–740	1.00	1.60
Overall	90–500	251	1–740	1.86	2.37

[a] λ, thermal conductivity; η, viscosity; NDP, number of data points; AAD %, $(1/\text{NDP}) \sum_i |\text{calculated} - \text{experimental})/\text{experimental}|_i$ 100%. Data source: Younglove et al. [12].

to calculate the parameters *a* and *b'* in the PR equation of state. These substance-dependent values are found in the critical book of Reid et al. [4]. The calculating procedure is to solve the PR equation of state to obtain the volume (or density) under certain temperature and pressures; then $b\rho$ and $b\rho\chi$ can be directly calculated with Eqs. (14) and (12). The viscosity coefficient and the thermal conductivity can be obtained simultaneously through Eqs. (15) and (19). This calculation procedure is simple and straightforward.

The parameters *A* and *D* are very important to the accuracy of predictions. It is found that parameter *A* can be treated as temperature and pressure independent and only substance dependent. But parameter *D* is temperature and substance dependent. The value of *D* is near unity for argon, compared to a range of 2 to 7 for propane. This can be seen

Table II. Comparisons of Calculated Results for Methane[a]

No.	T(K)	NDP	P, range (atm)	λ AAD %	η AAD %
1	115	15	1–98	0.72	
2	125	17	1–197	1.12	
3	135	16	1–197	1.28	
4	145	17	1–197	1.72	
5	170	17	1–20	0.45	
6	180	18	1–296	2.70	
7	200	16	1–150	2.33	
8	220	16	1–150	1.44	2.89
9	240	18	1–296	1.01	2.85
10	260	18	1–296	1.24	3.02
11	285	18	1–296	1.02	2.80
12	300	18	1–296	0.89	2.46
13	320	19	1–493	1.12	2.63
14	340	20	1–740	1.00	2.20
15	360	20	1–740	0.91	2.09
16	380	20	1–740	0.82	1.97
17	400	20	1–740	0.74	1.83
18	420	20	1–740	0.66	1.71
19	440	20	1–740	0.61	1.46
20	460	20	1–740	0.56	1.54
21	480	20	1–740	0.51	1.52
22	500	20	1–740	0.47	1.42
Overall	115–500	386	1–740	1.06	2.10

[a] λ, thermal conductivity; η, viscosity; NDP, number of data points; AAD %, $(1/\text{NDP}) \sum_i |(\text{calculated} - \text{experimental})/\text{experimental}|_i$ 100%. Data source: Hanley et al. [10].

Table III. Comparisons of Calculated Results for Ethane[a]

No.	T(K)	NDP	P, range (atm)	λ AAD %	η AAD %
1	340	17	1–197	2.75	2.85
2	360	18	1–296	1.96	2.76
3	380	18	1–296	0.87	2.86
4	400	19	1–493	0.96	2.63
5	420	19	1–493	1.26	2.40
6	440	19	1–493	1.49	2.30
7	460	19	1–493	1.94	2.29
8	480	19	1–493	2.17	2.19
9	500	19	1–393	2.33	2.08
Overall	340–500	167	1–493	1.75	2.48

[a] λ, thermal conductivity; η, viscosity; NDP, number of data points; AAD %, (1/NDP) $\sum_i$ |(calculated − experimental)/experimental|$_i$ 100 %. Data source: Hanley et al. [14].

Table IV. Comparisons of Calculated Results for Propane[a]

No.	T(K)	NDP	P, range (atm)	λ AAD %	η AAD %
1	140	21	1–493	0.59	
2	160	21	1–493	0.18	
3	180	21	1–493	0.36	
4	200	21	1–493	0.76	
5	220	21	1–493	1.15	
6	240	21	1–493	1.71	
7	260	21	1–493	2.13	
8	280	21	1–493	3.75	
9	360	21	1–493	2.36	
10	380	21	1–493	2.36	
11	400	21	1–493	2.94	4.51
12	420	21	1–493	1.65	3.79
13	440	21	1–493	1.44	3.68
14	460	21	1–493	1.98	3.61
15	480	21	1–493	2.34	3.41
16	500	21	1–493	2.72	3.25
Overall	140–500	336	1–493	1.78	3.71

[a] λ, thermal conductivity; η, viscosity; NDP, number of data points; AAD %, (1/NDP) $\sum_i$ |(calculated − experimental)/experimental|$_i$ 100 %. Data source: Hollan et al. [11].

obviously from Eq. (20), where M is dependent on substance and C_v is a function of temperature.

To test the prediction procedure proposed here, we have used the viscosity and thermal conductivity data for Ar, CH_4, C_2H_4, C_2H_6, and C_3H_8; all of the transport properties of these systems have been critically evaluated by a single group at NBS (Hanley et al. [10–14]) over the temperature range studied from low up to 500 K and pressure range from 1 to 750 atm. In the all cases the agreement between experiment and prediction is quite good, especially when one takes into account that the experimental uncertainty of the transport property data at high densities and that errors in the calculation of the density (i.e., by PR equation of state) are also reflected in the transport property predictions. The errors are increased as the critical point is approached. This is mainly because the PR equation of state cannot be used to describe the critical region; in other words, the pressure dependence of density in the critical region provided by the PR equation is incorrect.

As shown in Figs. 1 and 2, much better agreement with the experimental data is given by the modification of this work. In fact, for the typical system mathane the overall absolute average deviation in the predicted viscosity is only 2.07% and that in the thermal conductivity is 1.06% over a very large density range (from dilute gas to dense liquid) and 380 K

Table V. Comparisons of Calculated Results for Ethelene[a]

No.	T(K)	NDP	P, range (atm)	λ AAD %	η AAD %
1	280	10	1–20		2.27
2	300	13	1–20		3.17
3	320	16	1–40	5.39	3.22
4	340	20	1–60	5.19	3.51
5	360	21	1–89	4.92	3.13
6	380	21	1–98	4.73	2.98
7	400	21	1–97	4.57	2.79
8	420	21	1–197	4.41	2.53
9	440	21	1–296	4.27	2.23
10	460	21	1–394	4.06	1.95
11	480	21	1–483	3.88	1.70
12	500	21	1–493	3.61	1.49
Overall	265–500	227	1–493	4.50	2.55

[a] λ, thermal conductivity; η, viscosity; NDP, number of data points; AAD %, $(1/\mathrm{NDP}) \sum_i |(\mathrm{calculated} - \mathrm{experimental})/\mathrm{experimental}|_i$ 100%. Data source: Hollan et al. [13].

range in temperature (except those near the critical region). The results are better than the 2.36% for viscosity and 1.92% for thermal conductivity reported by Cohen and Sandler [6] using their correlations for the same data source but with a narrow temperature range (the temperature range is only 250 K in their work). All the predicted results are given in Tables I to V. The data reported in the literature are regular in interval of temperature and pressure. The range of the data used in this work are given in Tables I to V.

4. CONCLUSION AND DISCUSSION

Enskog theory is successfully combined with the PR equation of state in this work. It provides a unique and consistent predictive method for both transport properties and equilibrium properties. It is proved that this predictive method can be used to estimate the viscosity and thermal conductivity of pure fluids over a wide range of fluid states, from dilute gas to dense liquid. The calculation procedure is simple and straightforward. It requires only the critical temperature, critical pressure, and acentric factor of the substances.

The present method cannot be used in the region near the critical point. This inadequacy is due to two things: one is that the PR equation cannot be used in the critical region, and furthermore, none of the analytical equations of state can be used in the critical region [16], and another is that the Enskog theory does not account at all for the thermal conductivity anomaly in the critical region as discussed by Sengers [5].

The prediction procedure proposed here must be extended to a wider range of systems to generalize the correlation of parameters A and D. And it is also important to extend this procedure to mixtures for practical use in the engineering. The deviation of the predictions becomes large as the pressure become large. Some of the more accurate simple equations of state are expected to give better results. It is obvious that the proposed procedure is easy to extend to use with other equations of state.

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