

# Transport Properties of Refrigerant Mixtures: Thermal Conductivity

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**ABSTRACT:** *In the present work, the integral equations method is used to calculate transport properties of polar fluids. For this goal, we use the Stockmayer potential and examine theoretically the thermal conductivity of several refrigerant mixtures such as R125+R134a, R125+R32, R125+R152a, R134a+R32, R152a+R32, R134a+R143a, and R125+R143a. We solve numerically the Ornstein-Zernike (OZ) equation using the Hypernetted Chain (HNC) approximation for binary fluid mixtures and obtain the pair correlation functions. Finally, the temperature dependence of thermal conductivity is studied using Vesovic-Wakeham method and compared with available results.*

**KEY WORDS:** *Transport property, Thermal conductivity, Refrigerant mixtures, Binary mixtures.*

## INTRODUCTION

Understanding of structure and transport properties of molecular fluids, like viscosity and thermal conductivity, is one of main challenges in the condensed matter physics. Thermophysical properties of polar fluids have received much attention in past few years. Hitherto, the considerable progresses have been made in the understanding of the behavior of polar fluids by considering different models (*Hansen et al.* [1]; *Gray et al.* [2]). These models can be classified according to the type of interaction between the molecules (*Prera et al.* [3]; *Dijkstra et al.* [4]; *Moradi et al.* [5]; *Zhou et al.* [6]; *Gay et al.* [7]; *Khordad* [8]; *Papari et al.* [9]; *Khordad et al.* [10]).

There are a number of theoretical studies on the structure and the thermodynamic properties of polar fluids, and the existing theories can be classified into two different categories. The first one is based on Density Functional Theory (DFT), which has been applied quite

successfully to the simple and multi-component molecular fluids. The second one belongs to the methods based on the integral equation theory, which has been found to be quite successful in describing polar fluids. Integral equation theory for the structural and thermodynamic properties of molecular fluids with orientational degrees of freedom is now reasonably well developed (*Hansen et al.* [1]; *Gray et al.* [2]; *Blum* [11]; *Klapp et al.* [12]; *Wei et al.* [13]).

Wertheim's analytic solution (*Wertheim* [14]) of the mean spherical approximation integral equation for the dipolar hard sphere fluids was the first advance in our understanding of polar fluids since the work of *Onsager* [15]. Over the last two decades, integral equation method of classical equilibrium statistical mechanics have been used successfully to describe the thermodynamical properties and structure of simple and multi-component polar fluids such as dipolar hard spheres

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(Onsager [15]), the dipolar Yukawa (Henderson *et al.* [16]), dipolar hard ellipsoids (Perera *et al.* [17]), and the Stockmayer fluid (Rowlinson *et al.* [18]). It is worth mentioning that there is also another computational method to study polar fluids like the computer simulation.

As we know, the macroscopic properties of polar matter (in addition to dipole-dipole interaction) come from the balance between the short ranged atomic repulsions, which avoids the collapse, and the longer ranged attractions which keep the matter condensed. The theoretical models developed to study the properties of real systems have often included these two effects as separated pieces. One of the famous models is the Lennard-Jones (LJ) potential (Hansen *et al.* [1]; Khordad [8]; Papari *et al.* [9]).

Transport properties of polar fluids such as thermal conductivity and viscosity have been investigated using different theoretical (Hansen *et al.*, [1]; Gray *et al.* [2]) and computing simulation techniques (Allen *et al.* [19]; Frenkel *et al.* [20]; Sadus [21]; Alavi Fazel *et al.* [22]; Khorsand Movagar *et al.* [23]; Ziabasharhagh *et al.* [24]; Ghazanfari *et al.* [25]). A great deal of information for polar fluids has been obtained using the Stockmayer molecular model. Although that model is a great idealization of real polar molecules interactions, it has been used successfully for describing the properties of polar pure fluids (Hansen *et al.* [1]; Gray *et al.* [2]) and their mixtures (Rowlinson *et al.* [18]).

In the present work we apply an integral equation approach for obtaining transport properties of refrigerant mixtures using the Stockmayer model. For this purpose, we employ the Ornstein-Zernike (OZ) integral equation and HyperNetted Chain (HNC) closure relation for binary fluid mixtures. From a technical perspective, our approach essentially follows the methods developed for isotropic (Fries *et al.* [26]) and perfectly ordered systems in two and three dimensions (Caillol *et al.* [27]; Moradi *et al.* [28]). In order to solve the two-particle integral equations, all correlation functions are expanded in an appropriate angle-dependent basis set consisting of spherical harmonics. In this regard, we try to solve the OZ integral equation for binary fluid mixtures using the HNC approximation to find the correlation functions. Then, we apply these correlation functions to determine the thermal conductivity of several refrigerant mixtures

like R125+R134a, R125+R32, R125+R152a, R134a+R32, R152a+R32, R134a+R143a, and R125+R143a.

## THEORITICAL SECTION

### Stockmayer potential model

As we know, the description of the interaction between two molecules in polar fluids has greater problems than for spherical particles because the pair potential is a function both of the separation of the molecules and of their mutual orientation. Let us consider a system composed of spherical particles with an embedded point dipole at the center. The total pair potential between two molecules says *i* and *j*, separated by a distance

$$u(r_{ij}) = u^{LJ}(r_{ij}) + u^{dd}(r_{ij}) \quad (1)$$

Eq. (1) is called the Stockmayer potential model and it is the sum of the LJ potential

$$u_{ij}^{dd}(r_{ij}) = 4\epsilon_{ij} \left[ \left( \frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left( \frac{\sigma_{ij}}{r_{ij}} \right)^6 \right] \quad (2)$$

and the potential between two point dipoles, dipole-dipole (dd) interaction,  $\bar{\mu}_i$  and  $\bar{\mu}_j$  of strength  $\mu_i$  and  $\mu_j$  located at the centers of molecules *i* and *j*.

$$u_{ij}^{dd}(r_{ij}) = \left[ \frac{\bar{\mu}_i \cdot \bar{\mu}_j}{r_{ij}^3} - \frac{3(\bar{\mu}_i \cdot r_{ij})(\bar{\mu}_j \cdot r_{ij})}{r_{ij}^5} \right] \quad (3)$$

$$= \frac{\mu_i \cdot \mu_j}{r_{ij}^3} \left[ \bar{\mu}_i \cdot \bar{\mu}_j - 3(\hat{\mu}_i \cdot \hat{r}_{ij})(\hat{\mu}_j \cdot \hat{r}_{ij}) \right]$$

Also,  $\epsilon_{ij}$  sets the energy scale (the LJ energy parameter) and  $\sigma_{ij}$  the length scale (the LJ size parameter). To use the Stockmayer potential for polar mixtures, three parameters,  $\sigma_{ij}$ ,  $\epsilon_{ij}$  and  $\mu_{ij}$  must be determined. Therefore, the pure substance parameters are used to evaluate these parameters. In this case, we take the parameters,  $\sigma$ ,  $\epsilon$  and  $\mu$  from experimental data or simulation results. The dipole moment  $\mu$  is also taken directly from its experimental value. For the dipole moment parameter, we use effective Stockmayer potential model which has been reported by Gao *et al.* [29].

### Integral equation method

#### Expansion of the correlation functions

The whole structural information about the systems is contained in the total and direct correlation functions  $h(1,2)$  and  $c(1,2)$ . These are calculated by iterative solution of the OZ equation combined with a closure equation relating  $c(1,2)$ ,  $h(1,2)$  and the pair potential. The OZ equation for perfectly ordered binary mixtures is given by (Hansen *et al.* [1]).

$$h_{ij}(1,2) = c_{ij}(1,2) + \frac{1}{4\pi} \sum_{s=1}^2 d^3 h_{is}(1,3) \rho_s c_{sj}(3,2) \quad (4)$$

where  $\rho_s$  is the number density of species  $s$ ,  $c_{ij}$  and  $h_{ij}$  are the direct and total correlation functions between molecules of species  $i$  and  $j$ . There are few numerical results for the fluid mixtures with the help of the integral equation (4) combined with an appropriate closure relation (Khordad [8]; Moradi *et al.* [28]). Here, we give the basis steps to solve the OZ equation for the binary fluid mixtures using the Stockmayer model. Following Edmonds (Edmonds 1960 [30]), we treat the angle dependence of the two-particle correlation functions by expanding in a symmetry adapted basis set. We expand the correlation functions in terms of a complete set of angular functions. As we know, the correlation functions must be independent of our choice of coordinate system and this invariance simplifies the expansion. Introducing the variable  $\vec{r}_{12} = (\omega_{12}, r_{12}) = \vec{r}_2 - \vec{r}_1$  we find (Edmonds 1960 [30])

$$f_{ij}(1,2) = \sum_{l_1 l_2 l} f_{ij}(l_1 l_2 l; r_{12}) \Phi^{l_1 l_2 l}(\omega_1, \omega_2, \omega_{12}) \quad (5)$$

with  $f_{ij}(1,2) = h_{ij}(1,2)$  or  $c_{ij}(1,2)$  and

$$\Phi^{l_1 l_2 l}(\omega_1, \omega_2, \omega_{12}) = \quad (6)$$

$$\sum_{m_1 m_2 m} (-1)^{m_1} \begin{pmatrix} l_1 & l_2 & l \\ -m_1 & m_2 & m \end{pmatrix} Y_{l_1 m_1}^*(\omega_1) Y_{l_2 m_2}(\omega_2) Y_{lm}(\omega_{12})$$

Here  $\omega_{12} \equiv (\theta_{12}, \phi_{12})$  describes the orientation of  $r_{12}$ ,  $Y_{lm}(\omega)$  is a spherical harmonic, and

$$\begin{pmatrix} l_1 & l_2 & l \\ -m_1 & m_2 & m \end{pmatrix} \text{ is the } 3j \text{ symbol which relates to the}$$

Clebsch-Gordan coefficients (Gray *et al.*, 1984 [2]). Due to the properties of the dipolar potential, we have

$$f_{ij}^{l_1 l_2 l}(r) = f_{ij}^{l_2 l_1 l}(r)$$

#### The OZ integral equation

To treat the OZ equation (4) one introduces the Fourier transforms

$$\tilde{f}_{ij}(\mathbf{k}, \omega_1, \omega_2) = \int d\mathbf{r} e^{i\mathbf{k}\cdot\mathbf{r}} f_{ij}(r, \omega_1, \omega_2) = \quad (7)$$

$$\sum_{l_1 l_2 l} \tilde{f}_{ij}^{l_1 l_2 l}(\mathbf{k}) \Phi^{l_1 l_2 l}(\omega_1, \omega_2, \omega_{\mathbf{k}})$$

where  $\omega_{\mathbf{k}}$  describes the orientation of the wave vector  $\mathbf{k}$ .

The expansion coefficients are Hankel transforms (Gray *et al.* [2]) of the corresponding spatial functions defined by

$$\tilde{f}_{ij}^{l_1 l_2 l}(\mathbf{k}) = 4\pi i^l \int_0^\infty dr r^2 j_l(kr) f_{ij}^{l_1 l_2 l}(r) \quad (8)$$

Here  $j_l(kr)$  are spherical Bessel functions and  $i = \sqrt{-1}$ . In the following we will make use

of an alternative to Eq. (7): choosing the polar axis along  $\mathbf{k}$  one gets

$$\tilde{f}_{ij}(\mathbf{k}, \Omega_1, \Omega_2) = \sum_{l_1 l_2 l} \sum_{\lambda = -\min(l_1, l_2)}^{\lambda = \min(l_1, l_2)} \tilde{f}_{ij}^{l_1 l_2 \lambda}(\mathbf{k}) \Psi_\lambda^{l_1 l_2}(\Omega_1, \Omega_2) \quad (9)$$

Where

$$\Psi_\lambda^{l_1 l_2} = \frac{4\pi}{\sqrt{(2l_1 + 1)(2l_2 + 1)}} Y_{l_1 \lambda}(\Omega_1) Y_{l_2 \lambda}(\Omega_2) \quad (10)$$

Now,  $\Omega_1, \Omega_2$  describe orientations with respect to  $\mathbf{k}$  ( $\mathbf{k}$  frame) and the new coefficients are

linear combinations of those in the past system

$$\tilde{f}_{ij}^{l_1 l_2 \lambda}(\mathbf{k}) = \sum_{l = |l_1 - l_2|}^{l_1 + l_2} \sqrt{\frac{2l + 1}{4\pi}} C(l_1 l_2 l; \lambda, -\lambda, 0) \tilde{f}_{ij}^{l_1 l_2 l}(\mathbf{k}) \quad (11)$$

where  $C(l_1 l_2 l; \lambda, -\lambda, 0)$  is the Clebsch-Gordan coefficients. The coefficients have the properties (Hansen *et al.* [1]).

$$\tilde{f}_{ij}^{l_1 l_2 \lambda}(\mathbf{k}) = \tilde{f}_{ij}^{l_2 l_1 \lambda}(\mathbf{k}) \quad , \quad \tilde{f}_{ij}^{l_1 l_2 \lambda}(\mathbf{k}) = \tilde{f}_{ij}^{l_1 l_2, -\lambda}(\mathbf{k}) \quad (12)$$

The great advantage of the  $\mathbf{k}$  frame is that the OZ Eq. (4) decouples with respect to the

Index  $\lambda$ :

$$\tilde{h}_{ij}^{l_1 l_2 \lambda}(\mathbf{k}) = \tilde{c}_{ij}^{l_1 l_2 \lambda}(\mathbf{k}) + \quad (13)$$

$$\frac{1}{4\pi} \sum_{s=1}^2 \sum_{l=R}^2 \frac{(-1)^l}{2l_3 + 1} \tilde{h}_{is}^{l_1 l_2 \lambda}(\mathbf{k}) \rho_s \tilde{c}_{sj}^{l_1 l_2 \lambda}(\mathbf{k})$$

This equation can be written in matrix form for the values  $\lambda$  and  $k$ ,

$$\bar{h}_{ij}(\lambda; k) = \bar{c}_{ij}(\lambda; k) + \bar{h}_{is}(\lambda; k) \frac{\rho_s}{4\pi} \bar{c}_{sj} \bar{h}_{ij}(\lambda; k) \quad (14)$$

In above equation,  $\bar{c}_{ij}$  and  $\bar{h}_{ij}$  are  $2 \times 2$  matrices, where each element is a matrix with indices  $l_1$  and  $l_2$ . Also,  $\bar{\rho}_s$  is the diagonal matrix with indices  $\rho_1$  and  $\rho_2$ . This is a linear system of equations that determine  $\tilde{h}_{ij}^{l_1 l_2 \lambda}(k)$  if  $\tilde{c}_{ij}^{l_1 l_2 \lambda}(k)$  are known. As we see, this equation has two unknown functions. Therefore, we require an extra equation which relates these functions.

### Closure relationships

Closure expressions relate the two-particle correlation functions and the pair potential. In the present paper we consider the HNC approximation for the binary mixtures which can be written as (Hansen *et al.* [1])

$$c_{ij}(1, 2) = -\beta u_{ij}(1, 2) + h_{ij}(1, 2) - \ln g_{ij}(1, 2) \quad (15)$$

where  $\beta$  is the inverse temperature,  $g_{ij}$  is the pair distribution function, and  $u_{ij}$  is defined

in Eq. (1). A problem arises from the fact, that the logarithm in the closure [Eq. (15)] cannot be expanded in spherical invariants. This problem has been overcome by Fries & Patey [26]. By differentiating the closure with respect to one of independent variables one gets linear differential equations between the  $f_{ij}^{l_1 l_2 l}(r)$ .

Choosing the particle distance  $r_{12}$  as this variable yields (Fries *et al.* [26])

$$c_{ij}(1, 2) = \int_{r_{12}}^{\infty} dr' h_{ij}(1, 2) \frac{\delta W_{ij}(1, 2)}{\delta r'} - \beta u_{ij}(1, 2) \quad (16)$$

Where

$$W_{ij}(1, 2) = -y_{ij}(1, 2) - \beta u_{ij}(1, 2) \quad (17)$$

In above equation,  $y_{ij}(1, 2)$  is the auxiliary function between molecules of species  $i$  and  $j$ .

Employing this form of the closure together with Eq. (5) one obtains

$$c_{ij}^{l_1 l_2 m_1 m_2}(r) = \quad (18)$$

$$\sum_{l_1' l_2'} \sum_{m_1' m_2'} \sum_{l_1'' l_2''} \sum_{m_1'' m_2''} \int_r^{\infty} dr' h_{ij}^{l_1' l_2' m_1' m_2'}(r') \frac{\delta W_{ij}^{l_1'' l_2'' m_1'' m_2''}(r')}{\delta r'} - \beta u_{ij}^{l_1 l_2 m_1 m_2}(r)$$

where  $\wp$  depends on all the 15 indices and has the explicit form

$$\wp = \quad (19)$$

$$c(l_1' l_1'', 000) c(l_1' l_2' l_2'', 000) c(l_1'' l_1, 000) c(l_1' l_1', m_1' m_1' m_1) \times$$

$$c(l_2' l_2'', m_2' m_2'' m_2) c(l_1'' l_1, m' m'' m) \sqrt{\frac{(2l_1' + 1)(2l_1'' + 1)}{4\pi(2l_1 + 1)}}$$

$$\sqrt{\frac{(2l_2' + 1)(2l_2'' + 1)}{4\pi(2l_2 + 1)}}$$

with  $m = m_1' + m_1''$ ,  $m'' = m_1'' + m_2''$  and  $m = m_1 + m_2$ . This expansion, however, can only

be carried out numerically in most cases. With the help of this closure relation, we can now solve the OZ equation numerically by iteration (Khordad [8]; Fries *et al.* [26]; Moradi *et al.* [28]; Perera *et al.* [31]). In previous work (Khordad *et al.* [10]), we showed that at lower cutoff  $l_{\max} = 2$  the HNC closure gives different results for correlation functions which is not in agreement with computer simulations. But, at higher cutoff  $l_{\max} = 6$  the obtained results are in agreement with computer simulations. In the present work, we performed the calculations at lower cutoff, i.e., we truncated the series at  $l_{\max} = 2$ .

### Thermal conductivity

In order to put the subsequent discussion of the results in a proper context, it is useful to summarize the Vesovic-Wakeham (VW) prediction method. For brevity, only the essential elements of the methodology are presented here and the reader is referred to the original publication for more details (Dipippo *et al.* [32]; Sandler *et al.* [33]; Vesovic *et al.* [34]).

The most advanced theoretical results for the background thermal conductivity of dense fluid mixtures are those proposed by Mason *et al.* which are based upon the Thorne-Enskog equations for the transport properties of a fluid mixture or a gas mixture composed of  $N$  species of rigid spherical molecules. The results of Mason *et al.* can be written in the form [35]:

$$\lambda_{\text{mix}} = \lambda_{\text{mix}}(\text{mon}) + \lambda_{\text{mix}} \quad (20)$$

in which  $\lambda_{\text{mix}}(\text{mon})$  denotes the contribution of translational energy transport to the thermal conductivity and  $\lambda_{\text{mix}}(\text{mon})$  denotes the contribution of internal energy transport. Explicitly,

$$\lambda_{\text{mix}}(\text{mon}) = \frac{\begin{vmatrix} L_{11} & \cdots & L_{1N} & Y_1 \\ \vdots & & \vdots & \vdots \\ L_{N1} & \cdots & L_{NN} & Y_N \\ Y_1 & \cdots & Y_N & 0 \end{vmatrix}}{\begin{vmatrix} L_{11} & \cdots & L_{1N} \\ \vdots & & \vdots \\ L_{N1} & & L_{NN} \end{vmatrix}} + K_{\text{mix}}' \quad (21)$$

where

$$Y_i = x_i \left[ 1 + \sum_{j=1}^N \frac{2m_i m_j}{(m_i + m_j)^2} x_j \gamma_{ij} \bar{\chi}_{ij} \rho \right] \quad (22)$$

and

$$L_{ii} = \frac{x_i^2 \bar{\chi}_{ii}}{\lambda_{ij}^0} + \sum_{i \neq j} \frac{x_i x_j \bar{\chi}_{ij}}{2A_{ij}^* \lambda_{ij}^0 (m_i + m_j)^2} \times \quad (23)$$

$$\left[ \frac{15}{2} m_i^2 + \frac{25}{4} m_j^2 - 3m_j^2 B_{ij}^* + 4m_i m_j A_{ij}^* \right]$$

$$L_{ii} = \frac{x_i x_j m_i m_j}{2A_{ij}^* \lambda_{ij}^0 (m_i + m_j)^2} \left[ \frac{55}{4} - 3B_{ij}^* + 4A_{ij}^* \right] \quad (24)$$

$$K_{\text{mix}} = \frac{16}{5\pi} \frac{10}{9} \rho^2 \sum_{i=j}^N \sum_{j=1}^N \frac{x_i x_j m_i m_j}{(m_i + m_j)^2} \bar{\chi}_{ij} \gamma_{ij}^2 \lambda_{ij}^0 \quad (25)$$

$$\lambda(\text{int}) = \sum_{i=j}^N \left[ \frac{\lambda_i^0 - \lambda_{ij}^0(\text{mon})}{\bar{\chi}_{ii}} \right] \left[ 1 + \frac{x_j \lambda_i^0(\text{mon}) \bar{\chi}_{ij} A_{ii}^*}{x_i \lambda_i^0(\text{mon}) \bar{\chi}_{ii} A_{ij}^*} \right]^{-1} \quad (26)$$

Here  $\rho$  is the molar density of the fluid mixture, the quantities  $x_i$  and  $x_j$  are the mole fractions of species  $i$  and  $j$  and  $m_i$  and  $m_j$  are their molecular masses.  $A_{ij}^*$  and  $B_{ij}^*$  are weak functional of the intermolecular potential for the  $i$ - $j$  interaction.

The quantity  $\lambda_i^0$  displays the thermal conductivity of species  $i$  at zero density, and  $\lambda_i^0(\text{mon})$  is the translational contribution to the thermal conductivity of the same component. The symbol  $\lambda_{ij}^0(\text{mon})$  is the

interaction thermal conductivity for species  $i$  and  $j$ . The quantities  $\lambda_i^0(\text{mon})$  and  $\lambda_{ij}^0(\text{mon})$  can be obtained from the viscosity  $\eta_{ij}^0$  of dilute pure gases and the interaction viscosity  $\eta_{ij}^0$  according to the below equation

$$\lambda_{ij}^0(\text{mon}) = \frac{15k_B (m_i + m_j) \eta_{ij}^0}{8m_i m_j} \quad (27)$$

where  $k_B$  is the Boltzmann constant. The parameter  $\gamma_{ij}$  displays the shortening of the mean-free-path for interactions of species  $i$  and  $j$ , and  $\bar{\chi}_{ij}$  is the radial distribution function of species  $i$  and  $j$ .

We note that for the mixture thermal conductivity calculations, the pseudo-radial distribution function  $\bar{\chi}_{ij}$  for species  $i$  and  $j$  in the mixture should be evaluated. It is obvious that this quantity has an important role to determine the viscosity and thermal conductivity.

Related to this problem, various approximate theories (Moradi *et al.* [5]; Khordad [8]; Papari *et al.* [9]; Moradi *et al.* [28]; Perera *et al.* [31]; Degreve *et al.* [36]), and computer simulations have been carried out in two and three dimensions. As we know, in the most of earlier papers, the authors have used the Carnahan-Starling result to determine the viscosity and thermal conductivity some systems. Here, from the numerical solution of the OZ equation one can obtain  $c_{ij}(r)$  and  $h_{ij}(r)$ . Using the functions, we can obtain the radial distribution function.

From the numerical solution of the OZ equation one can obtain the radial distribution function and use in the thermal conductivity equations. To calculate the variables  $A_{ij}^*$  and  $B_{ij}^*$ , one can use the following relations (Royal *et al.* [37]; Royal *et al.* [38]).

$$\ln A_{ij}^* = 0.1281 - 0.1108 \ln T^* + 0.0962 (\ln T^*)^2 - \quad (28)$$

$$0.0271 (\ln T^*)^3 + 0.0024 (\ln T^*)^4$$

$$\ln B_{ij}^* = 1.1943596 - 0.13028165 \ln T^* + \quad (29)$$

$$0.019326273 (\ln T^*)^2 - 0.03207664 (\ln T^*)^3 -$$

$$0.014070309 (\ln T^*)^4 + 0.0015408879 (\ln T^*)^5$$

Where  $T^* = k_B T / \varepsilon_{ij}$  and

**Table 1: Molecular parameters for several refrigerant gases. ( $\varepsilon$  is the energy scale,  $\sigma$  is the length scale,  $\mu_{exp}$  is experimental dipole moment, and  $\mu^*$  effective dipole moment).**

Compound	Chemical formula	$\varepsilon/k_B T$	$\sigma$ (Å)	$\mu^*$	$\mu_{exp}$ (D)
R23	CHF	146.2	4.034	1.988	1.63
R32	CH <sub>2</sub> F <sub>2</sub>	163.1	3.900	2.098	1.98
R22	CHCLF <sub>2</sub>	199.8	4.374	1.768	1.46
R143a	CH <sub>3</sub> CF <sub>3</sub>	169.2	4.559	1.990	2.34
R152a	CHF <sub>2</sub> CH <sub>3</sub>	186.1	4.458	2.022	2.26
R125	CF <sub>3</sub> CHF <sub>2</sub>	166.7	4.727	1.979	1.56
R134a	CF <sub>3</sub> CH <sub>2</sub> F	174.9	4.632	2.084	2.06

$$\gamma_{ij} = \left( \frac{\gamma_{ii}^{1/3} + \gamma_{jj}^{1/3}}{8} \right)^3 \quad (30)$$

In Eq. (30), the parameter  $\gamma_{ii}$  can be determined from

$$\frac{\eta_i}{\eta_i^{(0)} \gamma_{ij} \rho^*} = 1 + \frac{2}{\sqrt{\beta'}} \quad (31)$$

where  $\eta_i^{(0)}$  is obtained from the experimental data.

## RESULTS AND DISCUSSION

There are few numerical results, theoretically, for the transport properties of polar fluid mixtures such as thermal conductivity. For this reason, we have selected several refrigerant mixtures like R125+R134a, R125+R32, R125+R152a, R134a+R32, etc. and tried to compute the thermal conductivity of these fluids by a numerical procedure. The main purpose of this work has been to solve numerically the OZ integral equation by using the HNC approximation and determine thermal conductivity of the mentioned particular fluids using the Vesovic-Wakeham (*Dipippo et al.* [32]; *Sandler et al.* [33]; *Vesovic et al.* [34]) procedure.

The pure substance parameters  $\sigma_{ii}$ ,  $\varepsilon_{ii}$ , and  $\mu_{ii}$  necessary in calculation of thermal conductivity were taken from Ref. 29. These parameters were listed in Table 1. In order to use the Stockmayer potential for the binary mixture systems and evaluate the thermal conductivity of them, we needed to know these parameters for mixtures.

Therefore, we have employed Lorentz-Berthelot combining rule to determine  $\sigma_{ij}$ ,  $\varepsilon_{ij}$ :

$$\varepsilon_{ij} = \sqrt{\varepsilon_{ii} \varepsilon_{jj}} \quad (32)$$

$$\sigma_{ij} = \frac{\sigma_{ii} + \sigma_{jj}}{2} \quad (33)$$

In addition, the dipole moments of mixtures were computed with the help of the following mixing rule:

$$\mu_{mix}^4 = \sigma_{mix}^3 \sum_{i=1} \sum_{j=1} \left( \frac{x_i x_j \mu_i^2 \mu_j^2}{\sigma_{ij}^2} \right) \quad (34)$$

where  $\mu_{mix}$  is dipole moment of mixture,  $x_i(x_j)$  is the mole fraction of species  $i(j)$  and  $\sigma_{ij}$  is defined in Eq. (33). Also,  $\sigma_{mix}$  is the length scale of mixture which can be written as

$$\sigma_{mix}^3 = \sum_{i=1} \sum_{j=1} x_i x_j \sigma_{ij}^3 \quad (35)$$

Table 2 shows the thermal conductivity of the binary mixture R125+R134a for different temperatures calculated at equal mole fractions. The obtained results have been compared with experimental results (*Moghadasi et al.* [39]). It is seen from the table that the thermal conductivity increases when temperature increases. We also see that the obtained results in this work are in fairly agreement with the experimental data. In Table 3, we have calculated the thermal

**Table 2: Temperature dependence of thermal conductivity of the binary mixture R125+R134a at equal mole fractions. Theoretical results ( $\lambda_{Th}$ ) have been compared with the experimental data ( $\lambda^{ex}$ ) (Moghadasi et al. [39]).**

T (K)	$10^3\lambda_{Th}$ (w/mK)	$10^3\lambda^{ex}$ (w/mK)	Error (%)
200	7.0461	7.829	10.000
250	9.855	10.950	10.000
273.15	11.272	12.525	10.004
300	12.991	14.435	10.003
373.15	17.973	19.970	10.000
473.15	25.195	27.995	10.002
523.15	28.562	32.092	11.000
673.15	39.704	44.115	10.000
723.15	42.692	47.968	11.001
873.15	52.935	58.816	10.001

**Table 3: Thermal conductivity of the binary mixture R125+R32 at different temperatures with equal mole fractions. Theoretical results ( $\lambda_{Th}$ ) have been compared with the experimental data ( $\lambda^{ex}$ ) (Moghadasi et al. [39]).**

T (K)	$10^3\lambda_{Th}$ (w/mK)	$10^3\lambda^{ex}$ (w/mK)	Error (%)
200	7.738	8.694	10.996
250	10.533	11.703	9.997
273.15	11.829	13.291	11.000
300	13.696	15.218	10.001
373.15	18.610	20.910	11.000
473.15	26.491	29.435	10.002
523.15	30.088	33.807	11.001
673.15	41.595	46.217	10.001
723.15	44.178	49.638	11.000
873.15	49.674	55.813	10.999

conductivity of R125+R32 at different temperatures with equal mole fractions. We have compared our results with the available experimental data (Moghadasi et al. [39]). In Tables IV to VII, thermal conductivity of several refrigerant mixtures like R125+R152a, R134a+R32, R134a+R143a, and R152a+R32 has been calculated at various temperatures for equal mole fractions. The results have been compared with the available

experimental results (Moghadasi et al. [39]). It should be noted that we have reported the computational errors in all tables. According to the obtained results, it is deduced that the thermal conductivity for all the binary mixtures (see Tables 2 to 7) is increased with enhancing temperature. Also, the calculated errors show that the agreement between our calculations and the experimental results is fairly good.

**Table 4: Thermal conductivity of the binary mixture R125+R152a at different temperatures with equal mole fractions. Theoretical results ( $\lambda_{Th}$ ) have been compared with the experimental data ( $\lambda^{ex}$ ) (Moghadasi et al. [39]).**

T (K)	$10^3\lambda_{Th}$ (w/mK)	$10^3\lambda^{ex}$ (w/mK)	Error (%)
200	7.289	8.190	11.001
250	10.197	11.330	10.000
273.15	11.555	12.983	10.999
300	13.362	15.014	11.003
373.15	18.864	20.960	10.000
473.15	26.838	29.820	10.000
523.15	30.571	34.349	10.999
673.15	43.467	48.297	10.001
723.15	47.677	52.975	10.001
873.15	58.664	65.915	11.001

**Table 5: Thermal conductivity of the binary mixture R134a+R143a at different temperatures with equal mole fractions. Theoretical results ( $\lambda_{Th}$ ) have been compared with the experimental data ( $\lambda^{ex}$ ) (Moghadasi et al. [39]).**

T (K)	$10^3\lambda_{Th}$ (w/mK)	$10^3\lambda^{ex}$ (w/mK)	Error (%)
200	7.519	8.448	10.997
250	10.26	11.429	10.228
273.15	11.728	13.031	9.999
300	13.529	15.032	9.999
373.15	18.841	20.934	9.998
473.15	26.485	29.758	10.999
523.15	30.766	34.184	9.999
673.15	41.490	46.618	11.000
723.15	45.041	50.045	9.999
873.15	49.501	55.619	11.000

## CONCLUSIONS

In the present work, we have first solved the OZ equation using the HNC closure relation for the Stockmayer potential. Next, we applied the Vesovic-Wakeham method to predict the thermal conductivity of several refrigerant mixtures. The pseudo-radial distribution functions needed for the thermal conductivity predictions were determined from the method on the

solution of the OZ equation by using the HNC closure relation. We have showed that the thermal conductivity of the Stockmayer fluid can be obtained relatively from integral equations method using the HNC closure relation. Using the Stockmayer potential model, we have evaluated and reported thermal conductivity values for several refrigerant mixtures such as R125+R134a, R125+R32, R125+R152a, R134a+R32, R134a+R143a,



**Table 6: Thermal conductivity of the binary mixture R134a+R32 at different temperatures with equal mole fractions. Theoretical results ( $\lambda_{Th}$ ) have been compared with the experimental data ( $\lambda^{ex}$ ) (Moghadasi et al. [39]).**

T (K)	$10^3\lambda_{Th}(w/mK)$	$10^3\lambda^{ex}(w/mK)$	Error (%)
200	7.076	7.951	11.005
250	9.786	10.996	11.004
273.15	11.338	12.598	10.002
300	12.990	14.596	11.003
373.15	18.506	20.562	9.999
473.15	26.491	29.349	9.738
523.15	30.123	33.846	11.000
673.15	42.303	47.003	9.999
723.15	45.559	51.190	11.000
873.15	56.636	62.929	10.000

**Table 7: Thermal conductivity of the binary mixture R152a+R32 at different temperatures with equal mole fractions. Theoretical results ( $\lambda_{Th}$ ) have been compared with the experimental data ( $\lambda^{ex}$ ) (Moghadasi et al. [39]).**

T (K)	$10^3\lambda_{Th}(w/mK)$	$10^3\lambda^{ex}(w/mK)$	Error (%)
200	8.039	9.033	11.004
250	10.750	12.079	11.003
273.15	12.355	13.728	10.001
300	14.069	15.808	11.001
373.15	19.960	22.178	10.001
473.15	28.518	32.043	11.001
523.15	33.555	37.283	9.999
673.15	46.310	52.034	11.000
723.15	50.530	56.144	9.999
873.15	56.904	63.937	11.000

and R152a+R32. The results are in fairly agreement with recent available results [35]. As can be seen from the obtained results in the tables, there is some difference for thermal conductivity associated with this method. Related to this difference, two points should be clarified: i) including all terms in Eq. (18) is not possible and hence the thermal conductivity cannot obtain exactly. ii) There are different functions in Eq. (18) which have various ranges. Hence, at higher temperatures, these functions have different values.

In summary, it is deduced that the integral equation method is suitable to predict transport properties of polar fluids like thermal conductivity.

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