JOURNAL OF THERMOPHYSICS AND HEAT TRANSFER
Vol. 14, No. 4, October–December 2000

Influence of Multipolar and Induction Interactions on the Speed of Sound

Jurij Avsec* and Milan Marčič†
University of Maribor, 2000 Maribor, Slovenia

At large distances between molecules, the intermolecular forces are essentially attractive. They can be classified conveniently into three types, that is, multipolar, induction, and dispersion forces. We consider rigid nonlinear molecules with enough symmetry so those principal axes of the quadrupole tensor of the polarizibility coincide. Multipolar and induction interactions are calculated with the help of quantum mechanical calculations of the intermolecular energy function and the help of perturbation theory. The multipole expansion is terminated at the quadrupole term. The focus is on the development of a mathematical model for calculation of the influence of multipole and induction interactions on the speed of sound and other thermodynamic functions of state. For the calculation of the thermodynamic functions of state, perturbation theory with the Lennard–Jones potential as the reference is used. The thermodynamic and structural properties of the Lennard–Jones system are known from Monte Carlo and molecular dynamics computer simulations. All important contributions are featured (translation, rotation, internal rotation, vibration, intermolecular potential energy, and the influence of electron and nuclei excitation). The analytical results are compared with the experimental data and models obtained by classical thermodynamics and show relatively good agreement.

Nomenclature

A = free energy, J
A^* = reduced free energy
a_i = coefficient to the Lennard–Jones part of free energy
b_i = coefficient of the Lennard–Jones contribution to the free energy
C_p = heat capacity at constant pressure per mole, J/kmolK
c_0 = speed of sound, m/s
d_i = coefficient of the QUACBACKONE and DIBACKONE equations
E = electric field, V/m
f = number of degrees of freedom
G = free enthalpy, J
G_i = coefficient of the Lennard–Jones contribution to the free energy
g = radial distribution function
H = enthalpy, J
$h, \hbar$ = Planck constant, Js
J = integral of pair correlation function
k = Boltzmann constant, J/K
k_i = coefficient of the QUACBACKONE and DIBACKONE equations
L = integral of triplet correlation function
M = molecular mass, kg/kmol
m_i = coefficient of the QUACBACKONE and DIBACKONE equations
N = number of molecules in system
n_i = coefficient of the QUACBACKONE and DIBACKONE equations
o_i = coefficient of the QUACBACKONE and DIBACKONE equations
P = pressure, Pa
P_l = Legendre function
p = momentum, N/s
q = molecule charge, C
q_p = charge density, C/m
R_m = universal gas constant, J/kmolK
r = intermolecular distance, m
S = entropy, J/K
T = temperature, K
T_p = reference temperature of the QUACBACKONE and DIBACKONE equations, K
T^* = reduced temperature
U = internal energy, J
u = intermolecular potential, J
V = volume, m^3
V_0 = reference volume of the QUACBACKONE and DIBACKONE equations, m^3
x_i = coefficient to the Lennard–Jones part of free energy
Z = partition function
α = polarization constant, m^3
β = element of multipole tensor, m
β_P = volumetric expansion coefficient, K^{-1}
γ = element of multipole tensor, m
γ_V = pressure coefficient, K^{-1}
δ = molecule moment, Nm
ε = Lennard–Jones parameter, J
ζ = element of multipole tensor, m
θ = quadrupole moment, Cm^2
θ^* = reduced quadrupole moment
μ = dipole moment, Cm
μ^* = reduced dipole moment
Ξ = Hamiltonian, J
ρ = number density, m^{-3}
ρ^* = reduced density
σ = Lennard–Jones parameter, m
ϕ_1 = internal angle at molecule 1, rad
χ_T = isothermal compressibility, bar^{-1}
ψ = molar fraction
ω = orientation of molecule, rad

Subscripts

att = attraction
conf = configuration

Presented as Paper 99-3677 at the AIAA 33rd Thermophysics Conference, Norfolk, VA, 28 June–1 July 1999; received 10 August 1999; revision received 27 April 2000; accepted for publication 25 May 2000.

[*] Mechanical Engineer, Department of Thermodynamics, Faculty of Mechanical Engineering, Smetanova 17. Member AIAA.

[†] Professor and Mechanical Engineer, Department of Thermodynamics, Faculty of Mechanical Engineering, Smetanova 17.

D = influence of dipole moments
el = influence of electron excitation
ir = internal rotation
nuc = influence of nuclear excitation
Q = influence of quadrupole moments
rep = repulsion
rot = rotation
trans = translation
vib = vibration
0 = ground state

Superscripts

disp = dispersion
ind = induction
mult = multipole moments
pert = perturbation
λ, $\lambda\lambda$, $\lambda\lambda\lambda$ = first-, second-, and third-order of perturbation

Introduction

THE calculation of the thermodynamic properties of state of refrigerants is exceptionally important in cooling system process design. In engineering practice, the cooling process calculation is most often carried out by means of charts, diagrams, or predesigned computer programs. Looking for thermodynamic quantities using diagrams and charts is extremely time consuming. With computer programs, on the other hand, the time required for data collection is substantially shortened, thus enabling us to calculate properties of some of the most frequently employed refrigerants, although computer programs allow only the calculation of certain thermodynamic properties, such as entropy, pressure, and enthalpy of a mixture. In practice we also often use equations of state (EOS) obtained through classical thermodynamics. Classical thermodynamics calculates the thermodynamic properties of state on the basis of macroscopic observation of substances. The equations obtained by means of classical thermodynamics are empirical and apply only in the region under observation. The main drawback of classical thermodynamics is that it lacks the insight into the substance microstructure. Contrary to classical thermodynamics, statistical thermodynamics calculates the thermodynamic properties of state on the basis of intermolecular and intramolecular interactions between particles in the same system of molecules. It deals with the systems composed of a very large number of particles. The main tasks of statistical thermodynamics is to derive thermodynamic laws and design a mathematical model for the calculation of macroscopic properties of matter.

In this paper we tried to calculate thermodynamic properties of state with the help of statistical thermodynamics.

The calculation of the thermodynamic functions of state for non-isotropic fluids is made possible by many statistical theories.[1–24] One of the most successful is perturbation theory with the Lennard–Jones fluid as the reference.[3,6,7]

To compare the accuracy of analytical models we often use numerical methods. The Monte Carlo method and the method of molecular dynamics have found particularly good application. In equilibrium thermodynamics the most favorable results are obtained by means of the Monte Carlo method.[1] Neither method is suitable for practical use because they require too much computer time. By means of modified thermal equations and approximate procedures, the results of numerical methods may be used to define the coefficients in the equations. The methods based on approximate procedures and numerical simulation are widely used in practical calculation of thermodynamic properties of state. Their great advantage over analytical models is mathematical simplicity.

Computation of Thermodynamic Properties of States

To calculate thermodynamic functions of state we applied the canonical partition.[25] The semi-classical formulation for the purpose of the canonical ensemble for N indistinguishable molecules can be expressed as follows[4]:

$$Z = \frac{1}{N!h^{Nf}} \times \int \ldots \int \exp\left(-\frac{\Xi}{kT}\right) \mathrm{d}\boldsymbol{r}_1\,\mathrm{d}\boldsymbol{r}_2, \ldots, \mathrm{d}\boldsymbol{r}_N\,\mathrm{d}\boldsymbol{p}_1\,\mathrm{d}\boldsymbol{p}_2, \ldots, \mathrm{d}\boldsymbol{p}_N \tag{1}$$

where Ξ is the Hamiltonian molecule system. The canonical ensemble for a system of N molecules can be represented by

$$Z = Z_0 Z_{\mathrm{trans}} Z_{\mathrm{vib}} Z_{\mathrm{rot}} Z_{\mathrm{ir}} Z_{\mathrm{el}} Z_{\mathrm{nuc}} Z_{\mathrm{conf}} \tag{2}$$

Thus the partition function Z is a product of terms of the ground state, the translation, the vibration, the rotation, the internal rotation, the influence of electron excitation, the influence of nucleus excitation, and the influence of the intermolecular potential energy. The canonical theory for computing the thermodynamic functions of the state can be represented as follows[26,27]:

$$P = kT\left(\frac{\partial \ln Z}{\partial V}\right)_{T,\psi}, \qquad U = kT^2\left(\frac{\partial \ln Z}{\partial T}\right)_{V,\psi}$$

$$S = k\left[\ln Z + T\left(\frac{\partial \ln Z}{\partial T}\right)_{V,\psi}\right]$$

$$H = kT\left[T\left(\frac{\partial \ln Z}{\partial T}\right)_{V,\psi} + V\left(\frac{\partial \ln Z}{\partial V}\right)_{T,\psi}\right]$$

$$G = -kT\left[\ln Z - V\left(\frac{\partial \ln Z}{\partial T}\right)_{V,\psi}\right], \qquad A = -kT\ln Z \tag{3}$$

Using Eq. (3) we can also calculate and express with the free energy some derived thermodynamic properties of state, which are very important in planning and monitoring the engineering processes:

$$C_P = \left(\frac{\partial H}{\partial T}\right)_{p,\psi} = -\left(\frac{\partial A}{\partial T}\right)_{V,\psi} - T\left(\frac{\partial^2 A}{\partial T^2}\right)_{V,\psi} - V\left[\frac{\partial}{\partial T}\left(\frac{\partial A}{\partial V}\right)_{T,\psi}\right]$$

$$\chi_T = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_{T,\psi} = \frac{1}{V}\left(\frac{\partial^2 V}{\partial A^2}\right)_{T,\psi}$$

$$\gamma_V = \frac{1}{P}\left(\frac{\partial p}{\partial T}\right)_{V,\psi} = \left(\frac{\partial V}{\partial A}\right)_{T,\psi}\left[\frac{\partial}{\partial T}\left(\frac{\partial A}{\partial V}\right)_{T,\psi}\right]_{V,\psi} \tag{4}$$

Let us try to find a connection between the pressure coefficient γ_V, volumetric expansion coefficient β_P, and isothermal compressibility χ_T:

$$\beta_P = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_{P,\psi} \tag{5}$$

$$\mathrm{d}V = \left(\frac{\partial V}{\partial T}\right)_{P,\psi}\mathrm{d}T + \left(\frac{\partial V}{\partial P}\right)_{T,\psi}\mathrm{d}P \tag{6}$$

$$\mathrm{d}P = \left(\frac{\partial P}{\partial V}\right)_{T,\psi}\mathrm{d}V + \left(\frac{\partial P}{\partial T}\right)_{V,\psi}\mathrm{d}T \tag{7}$$

When Eq. (6) is integrated into Eq. (7), we obtain

$$\mathrm{d}P = \left(\frac{\partial P}{\partial V}\right)_T \left[\left(\frac{\partial V}{\partial P}\right)_{T,\psi} \mathrm{d}P + \left(\frac{\partial V}{\partial T}\right)_{P,\psi} \mathrm{d}T\right] + \left(\frac{\partial P}{\partial T}\right)_{V,\psi} \mathrm{d}T \tag{8}$$

After rearranging the preceding equation, we can write

$$\beta_p = P \gamma_V \chi_T \tag{9}$$

The computation of the individual terms of the partition function and their derivatives, except for the configurational integral, is dealt with in various works.[3,25–27] In this paper we focus on the calculation of speed of sound. The term speed of sound refers to the speed of the mechanical longitudinal pressure waves propagating through a medium.[28] It is a very important parameter in the study of compressible fluids flows and in some applications of measurement (acoustic resonance level gauge).

The propagation of sonic waves for real fluids is almost in all cases nearly isentropic. Therefore, we can calculate the isentropic speed of sound for a real fluid c_0:

$$c_0 = \sqrt{-V^2 \left(\frac{\partial P}{\partial V}\right)_{S,\psi} \frac{1}{M}} \tag{10}$$

where ψ is molar concentration.

With help of the first and second law of thermodynamics, we can express the isentropic speed of sound:

$$\begin{aligned}
\mathrm{d}S &= \frac{C_P}{T}\mathrm{d}T - \left(\frac{\partial V}{\partial T}\right)_{P,\psi} \mathrm{d}P = 0 \\
&= \frac{C_P}{T} \cdot \left[\left(\frac{\partial T}{\partial V}\right)_{p,\psi} \cdot \mathrm{d}V + \left(\frac{\partial T}{\partial p}\right)_{V,\psi} \mathrm{d}P\right] \\
&\quad - \left(\frac{\partial V}{\partial T}\right)_{p,\psi} \mathrm{d}P = 0 \rightarrow \left(\frac{\partial P}{\partial V}\right)_{S,\psi} \\
&= \frac{C_P/T(\partial T/\partial V)_{p,\psi}}{(\partial V/\partial T)_{P,\psi} - C_P/T(\partial T/\partial P)_{V,\psi}}
\end{aligned} \tag{11}$$

$$\begin{aligned}
c_0 &= \sqrt{\frac{(-V^2/M)(C_P/T)(\partial T/\partial V)_{p,\psi}}{(\partial V/\partial T)_{p,\psi} - C_P/T(\partial T/\partial P)_{V,\psi}}} \\
&= \sqrt{-\frac{V C_P}{M T \beta_P(\beta_p V - C_P \beta_P / T \chi_T)}}
\end{aligned} \tag{12}$$

Therefore, the velocity of sound is a function of the thermodynamic properties of the fluid. It is evident from Eqs. (4–9) that all thermodynamical properties in Eq. (12) are expressed by free energy.

Intermolecular Potential

Molecules are composed of positive and negative charge. According to Coulomb's law of electrostatics, the charges interact and the interaction energy between the molecules in the system is called intermolecular energy. Hence, we say that intermolecular forces are of an electrostatic nature.

The analytical computation of intermolecular potential is extremely complex.[2,3,29,30] As far as certain simple systems are concerned, the problem is solvable, although the equations thus obtained are very complicated. This is why further analytical solution of a configuration integral is exceptionally difficult. In general, the assumption about the sum of repulsive and attractive forces is sufficiently accurate. If intermolecular potential is denoted by u, then it can be written as

$$u = u_{\mathrm{rep}} + u_{\mathrm{att}} \tag{13}$$

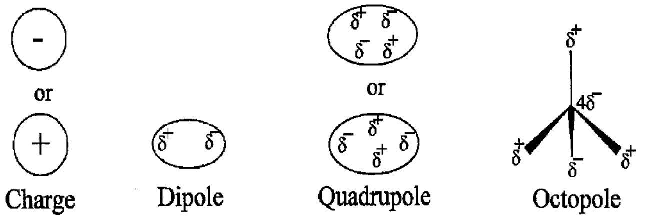

Fig. 1 Molecular multipole moments.

The occurrence of the repulsive force is associated with the Pauli exclusion principle. If two molecules approach one another within a very short distance, so that the electronic clouds of both molecules begin to coincide, certain electrons in the molecule have to move to higher energy levels due to the exclusion principle, made possible only through the supply of sufficient energy, resulting in the occurrence of the repulsive force.

Attractive intermolecular potential consists in general of three parts described next.

The first part is multipole or electrostatic force potential, which occurs due to the manifestation of static permanent dipole, quadrupole, and multipole moments or asymmetrical distribution of the charge in molecules. In this case the summation of Coulomb's interactions between positively charged nuclei and negatively charged electrons of a certain molecule with the adequate charge of another molecule gives, in general, a certain value of intermolecular energy. The interactions between molecules possessing multipole moments result in attractive forces, which are dependent on the orientation of the molecules in space. The distribution of charge can in general be described or denoted by multipole molecule moments. Figure 1 shows some of the lowest orders. A neutral atom with the negative cloud center of gravity coinciding with the center of gravity of a positive nucleus has a zero dipole moment. The first order of multipole moments is called a dipole moment and is created if the centers of gravity of positive and negative charge fail to coincide. It is represented by a partial positive and negative moment δ at a certain distance r, which creates the moment $r\delta$. In many cases the molecules have no dipole moments due to the symmetry of the charge. Nevertheless, they can have even higher orders of multipole moments, for example, quadrupole and octopole moments.

In general, multipole moments can be written as tensors[3] in the Cartesian coordinate system for the ζ, β, and γ elements of multipole tensors.

Molecule charge:

$$q = \int q_p \, \mathrm{d}\boldsymbol{r} \tag{14a}$$

Dipole:

$$\mu_\zeta = \int q_p \zeta \cdot \mathrm{d}\boldsymbol{r} \tag{14b}$$

Quadrupole:

$$\theta_{\zeta\beta} = \frac{1}{2} \int q_p \left(3\zeta\beta - r^2 \delta_{\zeta\beta}\right) \mathrm{d}\boldsymbol{r} \tag{14c}$$

Octopole:

$$\Omega_{\zeta\beta\gamma} = \frac{1}{2} \int q_p \left[5\zeta\beta\gamma - r^2(\varsigma\delta_{\beta\gamma} + \beta\delta_{\gamma\varsigma} + \gamma\delta_{\varsigma\beta})\right] \mathrm{d}\boldsymbol{r} \tag{14d}$$

where $\delta_{\zeta\beta} = 1$ if $\zeta = \beta$ and $\delta_{\zeta\beta} = 0$ if $\zeta \neq \beta$. Higher orders may be defined as well, but they are very rarely used in calculations.

The second part is induction force potential. The neutral atom with the negative electron cloud center of gravity coinciding with the center of gravity of the positive nucleus has no dipole moment. If, for example, such an atom is approached by another atom with a dipole moment, the dipole moment $\boldsymbol{\theta}_{\mathrm{ind}}$ is induced in the neutral atom, proportional to the electric field of the dipole moment $\boldsymbol{E}$:

$$\boldsymbol{\theta}_{\mathrm{ind}} = \alpha \boldsymbol{E} \tag{15}$$

This phenomenon is called redistribution of molecular charge or polarization. The redistribution of the molecular charge is shown in Fig. 2. The constant α is called the polarization constant. The polarization effect occurs also when two molecules with multipole moments approach one another.

In general, the polarization constant in a system of molecules with multipole moments is a tensor. The analytical calculation of tensor components of the polarization constant is very complex. In practical computations we usually satisfy ourselves with the mean polarization constant:

$$\alpha = \tfrac{1}{3}(\alpha_{xx} + \alpha_{yy} + \alpha_{zz}) \tag{16}$$

The electrostatic and inductive potentials occur in the case of polar molecules, where the potential energy is not dependent on the distance only, but also on the influence of the orientation of a molecule in space.

The third part is dispersion force potential. This occurs both in polar and nonpolar molecules. It results from time-varying dipole moments. In most cases the potential of dispersion forces represents the most important element. In general, an example of nonpolar molecules can be expressed by the following relation:

$$u_{\text{disp}} = \left(C_1/r^6\right) + \left(C_2/r^8\right) + \left(C_3/r^9\right) \tag{17}$$

where C_1, C_2, and C_3 are constants.

Table 1 illustrates the influence of multipole, dispersion, and inductive forces on thermodynamic properties of state at an intermolecular distance r. Note that Table 1 shows the impact of multipole, inductive, and dispersion forces varying considerably with different molecules of refrigerants. The influence of multipole forces is the highest with water as the refrigerant medium (R 718), representing even today one of the major problems in calculating the thermodynamic functions of state.

In general, one may establish the following points.

1) The effect of inductive forces is very low in almost all cases. With certain high-polar molecules, however, the effect of multipolar forces is very often the same magnitude as the dispersion forces.

2) The computation of thermodynamic properties of state using isotropic potentials is good enough for nonpolar and low-polar molecules.

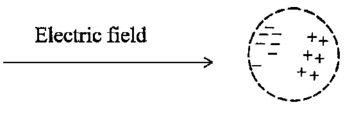

Fig. 2 Molecule polarization.

Table 1 Impact of molecular structure on multipole, inductive, and dispersion contribution[30]

		Interaction energy, kJ/mol		
Refrigerant	r, nm	Multipole	Inductive	Dispersion
R 740	0.37	——	——	−1.1
CO	0.40	——	−0.000006	−1.3
R 717	0.29	−6.2	−0.9	−12.9
R 718	0.30	−16.1	−0.9	−5.3

3) For the computation of thermodynamic properties of state of high-polar molecules, primarily in the area of liquids, the theory of anisotropic potentials needs to be taken into consideration.

Reference Intermolecular Potential

For the calculation of thermodynamical properties of state, the Lennard–Jones (LJ) fluid is the most widely used model. In our case, we used the LJ fluid as the reference model for the calculation of influences of multipolar and inductive interactions. To calculate the LJ fluid properties, the most widely used method in the engineering practice has been the modified Benedict–Webb–Rubin (BWR) thermal equation of state, containing 33 necessary constants,[31–34] of which 32 are linear coefficients x_i and one is also nonlinear γ. We used the results of Johnson et al.[34] [Johnson–Zollweg–Gubbins (JZG)], who provide, contrary to others,[31–33] more favorable results over the entire region. The JZG model perfectly discerns thermodynamic properties of state from the triple point to the four- and fivefold value of critical temperature and over the entire liquid–gas region. By means of the modified BWR thermal equation of state, the configuration contribution to the free energy can be written as

$$A^*_{\text{LJ}} = \sum_{i=1}^{8} \frac{a_i \rho^{*i}}{i} + \sum_{i=1}^{6} b_i G_i \tag{18}$$

In Eq. (18), A^*_{LJ} is reduced contribution to the configuration free energy, and

$$\rho^* = N\sigma^3/V, \qquad T^* = kT/\varepsilon$$

$$A^*_{\text{LJ}} = A_{\text{LJ}}/N\varepsilon, \qquad F = \exp(-\gamma\rho^{*2}) \tag{19}$$

The coefficients a_i, b_i, and G_i required for the calculation in Eq. (18) are given in Table 2.

Impact of Anisotropic Potentials on Thermodynamic Functions of States

Models that yielded favorable results in practical computations for a large number of components and within a relatively wide range of density and temperature were used.

The Müller–Winkellman–Fischer (MWF) (see Refs. 10–13) model deals with the influence of quadrupole and dipole moments on thermodynamic properties of state. The method is based on the assumption of nonindependence of dispersion forces, dipole, and quadrupole moments. Using this assumption, we can write that the free configuration energy of the system of molecules equals the sum of its individual parts:

$$A_{\text{conf}} = A_{\text{LJ}} + A_D + A_Q \tag{20}$$

In Eq. (20) A_{LJ} is the impact of the LJ fluid. The free energy of the LJ fluid A_{LJ} was calculated using the JZG model, that is, Eq. (18). A_D and A_Q are the influence of dipole and quadrupole moments on free energy. Here,

$$\mu^* = \mu\Big/\sqrt{\varepsilon\sigma^3}, \qquad \theta^* = \theta\Big/\sqrt{\varepsilon\sigma^5} \tag{21}$$

where the coefficients μ^* and θ^* are reduced dipole and quadrupole moments.

Table 2 Coefficients for calculation of the configuration contribution to free energy

i	a_i	b_i	G_i
1	$x_1T^* + x_2\sqrt{T^*} + x_3 + x_4/T^* + x_5/T^{*2}$	$x_{20}/T^{*2} + x_{21}/T^{*3}$	$(1 - F)/(2\gamma)$
2	$x_6T^* + x_7 + x_8/T^* + x_9/T^{*2}$	$x_{22}/T^{*2} + x_{23}/T^{*4}$	$-(F\rho^{*2} - 2G_1)/(2\gamma)$
3	$x_{10}T^* + x_{11} + x_{12}/T^*$	$x_{24}/T^{*2} + x_{25}/T^{*3}$	$-(F\rho^{*4} - 4G_2)/(2\gamma)$
4	x_{13}	$x_{26}/T^{*2} + x_{27}/T^{*4}$	$-(F\rho^{*6} - 6G_3)/(2\gamma)$
5	$x_{14}T^* + x_{15}/T^{*2}$	$x_{28}/T^{*2} + x_{29}/T^{*3}$	$-(F\rho^{*8} - 8G_4)/(2\gamma)$
6	x_{16}/T^*	$x_{30}/T^{*2} + x_{31}/T^{*3} + x_{32}/T^{*4}$	$-(F\rho^{*10} - 10G_5)/(2\gamma)$
7	$x_{17}/T^* + x_{18}/T^{*2}$	——	——
8	x_{19}/T^{*2}	——	——

The influence of the dipole moments is

$$\frac{A_D}{R_m T} = \sum_{i=1}^{28} d_i \left(\frac{T}{T_p}\right)^{n_i/2} \left(\frac{V_0}{V}\right)^{m_i/2} \left(\mu^{*2}\right)^{k_i/4} \exp\left[-o_i\left(\frac{V_0}{V}\right)^2\right] \tag{22}$$

which is called the DIBACKONE equation. Coefficients V_0 and T_p are determined for each component separately, and coefficients n_i, m_i, d_i, k_i, and o_i are presented in the literature.[10]

The influence of the quadrupole moments is

$$\frac{A_Q}{R_m T} = \sum_{i=1}^{17} d_i \left(\frac{T}{T_p}\right)^{n_i/2} \left(\frac{V_0}{V}\right)^{m_i/2} \left(\theta^{*2}\right)^{k_i/4} \exp\left[-o_i\left(\frac{V_0}{V}\right)^2\right] \tag{23}$$

which is called the QUACKBACKONE equation. Coefficients n_i, m_i, d_i, k_i, and o_i are presented in the literature.[10]

The Lucas–Gubbins model (see Refs. 3, 6, and 24) deals with the perturbation expansion around the LJ intermolecular potential. The total intermolecular potential can be written as a sum of the LJ intermolecular potential and the potential that also takes into account the orientation of a molecule in space:

$$u_{12}(r_{12}, \omega_1, \omega_2) = u_{\mathrm{LJ}_{12}}(r_{12}) + u_{\mathrm{pert}_{12}}(r_{12}, \omega_1, \omega_2) \tag{24}$$

where r_{12} is the distance between the centers of gravity for molecules 1 and 2 and ω_1 and ω_2 are orientations of both molecules in space, which may be expressed with Euler's angles. The reference part u_{LJ} can also be written as a certain mean intermolecular energy at the distance r_{12}:

$$u_{\mathrm{LJ}_{12}}(r_{12}) = \langle u_{12}(r_{12}, \omega_1, \omega_2)\rangle_{\omega_1\omega_2} = \frac{\int u_{12}(r_{12}, \omega_1, \omega_2)\,\mathrm{d}\omega_1\,\mathrm{d}\omega_2}{\int \mathrm{d}\omega_1\,\mathrm{d}\omega_2} \tag{25}$$

Now suppose that the sum of intermolecular potential energy is

$$U_{\mathrm{conf}} = \sum_{i<j} u_{ij} = \sum_{i<j} u_{\mathrm{LJ}_{ij}}(r_{ij}) + \sum_{i<j} u_{ij}^{\mathrm{pert}}(r_{ij}, \omega_i, \omega_j) \tag{26}$$

Using the perturbation expansion around the reference potential, one can then write the configuration effect on the free energy as

$$\begin{aligned}(A_{\mathrm{conf}}/NkT) &= (A_{\mathrm{LJ}}/NkT) + (A^{\lambda}/NkT)\\ &\quad + (A^{\lambda\lambda}/NkT) + (A^{\lambda\lambda\lambda}/NkT)\end{aligned} \tag{27}$$

The free energy of the LJ fluid A^{LJ} was calculated using the JZG model, that is, Eq. (18).

We consider rigid nonlinear molecules[3] with enough symmetry so that the principal axes of the quadrupole tensor coincide. The multipole expansion is terminated at the quadrupole term. Intermolecular repulsion interaction is modeled by the LJ r^{-12} law. The induction interactions are formulated in the isotropic polarizibility approximation. Intermolecular interactions are limited to the second-order term, and cross terms between intermolecular interactions are not considered.

Much recent academic study in molecular thermodynamics has been directed toward more complex theories without adequate attention to how such theories may be used in practical thermodynamics. This simplified model is a compromise between the analytical models from the literature[2,3,6] and the technically important resolution of mathematical problems, which allows the calculation of thermodynamic properties of state of interesting refrigerants and the impact of anisotropic effects on the speed of sound.

The configurational free energy is given as follows. The first-order terms are the inductive forces:

$$\begin{aligned}\left(\frac{A^{\lambda}}{NkT}\right)^{\mathrm{ind}} &= -4\pi\frac{N}{V}\left(\frac{1}{kT}\right)\alpha\left[\left(\mu_x^2 + \mu_y^2 + \mu_z^2\right)\frac{J(6)}{\sigma^3}\right.\\ &\quad \left. + \left(\theta_x^2 + \theta_y^2 + \theta_z^2\right)\frac{J(8)}{\sigma^5}\right]\end{aligned} \tag{28}$$

The second-order terms consist of multipole forces:

$$\begin{aligned}\left(\frac{A^{\lambda\lambda}}{NkT}\right)^{\mathrm{mult-mult}} &= -\frac{\pi N}{(kT^2)V}\left[\frac{2}{3}\left(\mu_x^2 + \mu_y^2 + \mu_z^2\right)^2\frac{J(6)}{\sigma^3}\right.\\ &\quad + \frac{4}{3}\left(\mu_x^2 + \mu_y^2 + \mu_z^2\right)\left(\theta_x^2 + \theta_y^2 + \theta_z^2\right)\frac{J(8)}{\sigma^5} + \frac{56}{45}\left(\mu_x^2 + \mu_y^2\right.\\ &\quad \left.\left. + \mu_z^2\right)\left(\theta_x^2 + \theta_y^2 + \theta_z^2\right)\frac{J(10)}{\sigma^7}\right]\end{aligned} \tag{29}$$

and inductive forces:

$$\left(\frac{A^{\lambda\lambda}}{NkT}\right)^{\mathrm{ind-ind}} = \left(\frac{A^{\lambda\lambda}}{NkT}\right)_A^{\mathrm{ind-ind}} + \left(\frac{A^{\lambda\lambda}}{NkT}\right)_B^{\mathrm{ind-ind}}$$

$$\begin{aligned}\left(\frac{A^{\lambda\lambda}}{NkT}\right)_A^{\mathrm{ind-ind}} &= -\frac{9N\pi}{V(kT)^2}\alpha^2\left[\frac{2}{45}\left(\mu_x^2 + \mu_y^2 + \mu_z^2\right)^2\frac{J(12)}{\sigma^9}\right.\\ &\quad + \frac{24}{25}\left(\mu_x^2\theta_x^2 + \mu_y^2\theta_y^2 + \mu_z^2\theta_z^2\right)\frac{J(14)}{\sigma^{11}} + \frac{32}{315}\left(\mu_x^2 + \mu_y^2 + \mu_z^2\right)^2\\ &\quad \times\left(\theta_x^2 + \theta_y^2 + \theta_z^2\right)\frac{J(14)}{\sigma^{11}} + \frac{1024}{4725}\left(\mu_x^2\theta_x^2 + \mu_y^2\theta_y^2 + \mu_z^2\theta_z^2\right.\\ &\quad \left. - \frac{5}{8}\mu_x^2\theta_z\theta_y - \frac{5}{8}\mu_y^2\theta_x\theta_z - \frac{5}{8}\mu_z^2\theta_x\theta_y\right)\frac{J(14)}{\sigma^{11}}\\ &\quad \left. + \frac{24}{315}\left(\theta_x^2 + \theta_y^2 + \theta_z^2\right)^2\frac{J(16)}{\sigma^{13}}\right]\end{aligned} \tag{30}$$

$$\begin{aligned}\left(\frac{A^{\lambda\lambda}}{Nk_BT}\right)_B^{\mathrm{ind-ind}} &= -\frac{9\pi^2N^2}{(VkT)^2}\sigma^2\alpha^2\left[\frac{48}{25}\left(\mu_x^2\theta_x^2 + \mu_y^2\theta_y^2 + \mu_z^2\theta_z^2\right)\right.\\ &\quad \times\frac{L(1,7,7)}{\sigma^{10}} + \frac{4}{45}\left(\mu_x^2 + \mu_y^2 + \mu_z^2\right)\frac{L(2,6,6)}{\sigma^8} + \frac{64}{315}\left(\mu_x^2\right.\\ &\quad \left. + \mu_y^2 + \mu_z^2\right)\left(\theta_x^2 + \theta_y^2 + \theta_z^2\right)\frac{L(2,6,8)}{\sigma^{10}} + \frac{256}{2205}\left(\theta_x^2 + \theta_y^2 + \theta_z^2\right)\\ &\quad \times\frac{L(2,8,8)}{\sigma^{12}} + \frac{2048}{4725}\left(\mu_x^2\theta_x^2 + \mu_y^2\theta_y^2 + \mu_z^2\theta_z^2 - \frac{5}{8}\mu_x^2\theta_z\theta_y\right.\\ &\quad \left. - \frac{5}{8}\mu_y^2\theta_x\theta_z - \frac{5}{8}\mu_z^2\theta_x\theta_y\right)\frac{L(3,7,7)}{\sigma^{10}} + \frac{16}{441}\left(\theta_x^2 + \theta_y^2 + \theta_z^2\right)^2\\ &\quad \left.\times\frac{L(4,8,8)}{\sigma^{12}}\right]\end{aligned} \tag{31}$$

The structural properties of the LJ potential are introduced via the J and L integrals expressed as

$$\begin{aligned}J(n) &= \int_0^\infty \frac{1}{r^{*n}} g_{\mathrm{LJ}} r^{*2}\cdot \mathrm{d}r^*\\ L(l; n, n') &= \int_0^\infty\int_0^\infty\int_{-1}^1 P_l(\cos\phi_1)\\ &\quad \times g_{\mathrm{LJ}_3} r_{12}^{*(2-n)} r_{13}^{*(2-n')}\,\mathrm{d}r_{12}^*\,\mathrm{d}r_{13}^*\,\mathrm{d}(\cos\phi_1)\end{aligned} \tag{32}$$

$$r^* = r/\sigma$$

where g_{LJ} and g_{LJ_3} are pair and triplet radial distributions function[3] for the LJ potential, $P_l(\cos\phi_1)$ is the Legendre function, and ϕ_1 is the internal angle at molecule 1 for the triangle formed by molecules 1, 2, and 3.

The J and L integrals are calculated by numerical integration over tabulated pair correlation functions. We calculated the J and

Table 3 Constants necessary for calculation of speed of sound

	LJ parameters			Reduced multipole moments			
				LG model (LGa and LGb)		MWF model	
Mixture	$\sigma = 10^{10}$ m	$\varepsilon = 10^{21}$ J	Polarization constant = $\alpha 10^{30}$ m^3	μ^*	θ^*	μ^*	θ^*
R 290	4.51	4.27	——	——	$\theta_z^* = -0.86$	——	-1.28
R 50	3.76	2.05	2.5	——	——	——	——
R 744	3.94	2.69	2.7	——	$\theta_x^* = 0.88, \theta_z^* = 1.09$	——	-2.815
R 717	2.92	7.52	2.4	$\mu_z^* = -1.4$	$\theta_z^* = -0.588$	-3.03	-1.93

L integrals with the help of simple interpolation equations from Ref. 31, labeled LGa, and Ref. 14, labeled LGb.

Mixtures

The thermodynamic properties of real mixtures are obtained using the one-fluid theory.[6,35] The molecules interacting with LJ potential have parameters σ and ε given by

$$\sigma^3 = \sum_{i,j} \psi_i \psi_j \sigma_{ij}^3, \qquad \varepsilon\sigma^3 = \sum_{i,j} \psi_i \psi_j \varepsilon_{ij} \sigma_{ij}^3 \tag{33}$$

$$\sigma_{ij} = (\sigma_{ii} + \sigma_{jj})/2, \qquad \varepsilon_{ij} = \sqrt{\varepsilon_{ii}\varepsilon_{jj}} \tag{34}$$

We calculated all other important parameters with the help of the following mixing rule. For some general parameter K we can write

$$K = \sum_i \psi_i K_i \tag{35}$$

Results and Discussion

We have carried out the calculations for propane R 290 (C_3H_8), a mixture of 70% methane R 50 (CH_4) and 30% carbon dioxide R 744 (CO_2), and ammonia R 717 (NH_3). Table 3 shows some important constants needed for the calculation of the speed of sound on the basis of statistical thermodynamics. The constants necessary for computation, such as LJ parameters, polarization constant and reduced multipole moments, are obtained from data[2–4,6,10–13,21,25] and from comparison between analytical and experimental results. The comparison of our calculations with the models obtained by classical thermodynamics [Jacobsen–Stewart model (JS) (Jacobsen et al.[36]) BWR EOS,[37] Benedict–Webb–Rubin–Starling–Nishiumi (BWRSN) EOS (see Refs. 38 and 39)] and experimental thermodynamic data from the literature[40–42] is presented in Tables 4–9 and Figs. 3 and 4.

The BWR EOS is the most widely used EOS in practical calculations. It calculates very accurately the thermodynamic properties of real gases, though it is not sufficiently accurate for the region of real liquids. The equation contains eight constants and provides very good results for simple molecules over the entire range of pressure and temperature. The BWRSN thermal equation is applicable also for calculation in the region of liquids. It contains 15 constants and also the influence of the polar molecules. The JS EOS contains up to 100 constants. Today, the JS model is one of the most accurate models and is suitable for the calculation of properties of polar molecules both in the gaseous and liquid regions. Unfortunately, the model in its present form cannot easily be applied to the calculation of thermodynamic properties in mixtures.

Tables 4 and 5 show the deviation of the speed of sound for saturated propane for the real gas region between the analytical results obtained by the models on the basis of isotropic statistical thermodynamics (JZG), nonisotropic statistical thermodynamics (JZG–MWF, JZG–LGa, and JZG–LGb), the complex JS model using classical thermodynamics, and thermodynamic data.[40,41] The analytical results obtained by statistical thermodynamics show very good agreement.

Table 4 Speed of sound c_0 for R 290 (saturated vapor)

	T, K					
Model	223	243	283	323	343	AAD
JS	217	220	219	201	183	0.005973
JZG	217	221	215	193	166	0.033965
JZG-MWF	217	220	217	198	173	0.018633
JZG–LGa	217	220	218	201	186	0.017296
JZG–LGb	217	220	218	202	185	0.004856
Experiment[40,41]	215	219	218	201	184	——

Table 5 AD for R 290 (saturated vapor)

	T, K				
Model	223	243	283	323	343
JS	0.009302	0.004566	0.004587	0	0.005435
JZG	0.009302	0.009132	0.013761	0.039801	0.097826
JZG-MWF	0.009302	0.004566	0.004587	0.014925	0.059783
JZG–LGa	0.00186	0.004566	0	0	0.01087
JZG–LGb	0.009302	0.004566	0	0.004975	0.005435

Table 6 Comparison between analytical results and experimental speed of sound data for 70% R 50/30% R 744 mixture at 250 K

Model	10 bar	20 bar	60 bar	100 bar	AAD, %
JZG	329	323	301.6	300	0.022364
BWR	332.4	315.2	277.5	272.1	0.047959
BWRSN	332.3	314.9	282.9	323.7	0.021633
JZG–LGa	329.8	323	288.8	313.1	0.006061
Experiment[42]	329	319	290	311.5	——

Table 7 Influence of ARVS for 70% R 50/30% R 744 mixture with JZG–LGa model

T, K	10 bar	20 bar	60 bar	100 bar
250	0.002432	0.000929	0.04244	0.043667
300	0	0.000279	0.001141	0.000859
350	0	0	0.00026	0.000517

Analytical results are presented also as a function of the average absolute deviation (AAD) where

$$\text{AAD} = \sum \left| \frac{(\text{data}_{\text{exp}} - \text{data}_{\text{calc}})}{\text{data}_{\text{exp}}} \right| \Big/ \text{number of points}$$

(Table 4) and the absolute deviation (AD) where

$$\text{AD} = \sum \left| \frac{(\text{data}_{\text{exp}} - \text{data}_{\text{calc}})}{\text{data}_{\text{exp}}} \right| \tag{36}$$

(Table 5) depending on the temperature. Figure 3, showing the effect of nonisotropic interactions by means of the absolute ratio of the speed of sound (ARVS), is especially interesting:

$$\text{ARVS} = \text{ABS}\left(\frac{c_{0_{\text{nonisotropic}}} - c_{0_{\text{isotropic}}}}{c_{0_{\text{isotropic}}}} \right) \tag{37}$$

where $c_{0_{\text{isotropic}}}$ is the speed of sound obtained based on the LJ (JZG) model.

As is evident from Fig. 3, the effect of nonisotropic interactions on the speed of sound in the region of higher pressure can exceed 10%.

Table 8 Speed of sound c_0 for R 717 (saturated vapor)

		Model					
T, K	V, m^3/kmol	Experiment[40]	JS	BWRSN	JZG	JZG–LGa	JZG–MWF
223	44.7600	376.20	377.00	375.70	377.90	377.90	374.40
243	16.3700	389.60	389.30	389.60	390.80	390.60	387.30
263	7.0720	399.60	398.16	401.20	400.60	400.70	398.80
283	3.5020	406.80	403.30	410.00	406.00	406.70	408.40
303	1.8530	410.00	404.50	403.00	404.80	407.30	408.40
323	1.0670	409.20	414.70	414.00	395.80	403.00	414.70
343	0.6430	402.90	401.40	409.00	374.70	394.10	416.70
363	0.3950	388.80	379.10	398.10	332.40	384.60	411.00
373	0.3090	377.20	369.40	390.70	296.50	384.50	368.80
AAD	——	——	0.0101	0.0129	0.0540	0.0093	0.0164

Table 9 AD of speed of sound for R 717 (saturated vapor)

		Model				
T, K	V, m^3/kmol	JS	BWRSN	JZG	JZG–LGa	JZG–MWF
223.0	44.7600	0.0021	0.0013	0.0045	0.0045	0.0048
243.0	16.3700	0.0008	0.0000	0.0031	0.0026	0.0059
263.0	7.0720	0.0036	0.0040	0.0025	0.0028	0.0020
283.0	3.5020	0.0086	0.0079	0.0020	0.0002	0.0039
303.0	1.8530	0.0134	0.0171	0.0127	0.0066	0.0039
323.0	1.0670	0.0134	0.0117	0.0327	0.0152	0.0134
343.0	0.6430	0.0037	0.0151	0.0700	0.0218	0.0343
363.0	0.3950	0.0249	0.0239	0.1451	0.0108	0.0571
373.0	0.3090	0.0207	0.0358	0.2139	0.0194	0.0223

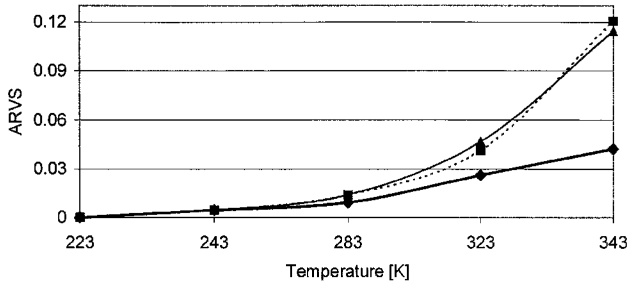

Fig. 3 Influence of multipolar and induction forces on the speed of sound for R 290: ◆, JZG–MWF; ■, JZG–LGa; and ▲, JZG–LGb.

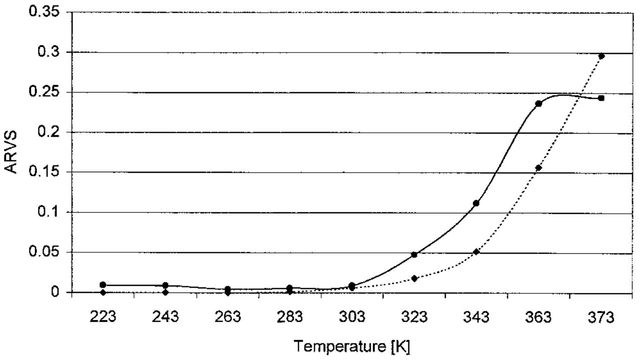

Fig. 4 Influence of multipolar and induction forces on the speed of sound for R 717: ◆, JZG–LGa, and ●, JZG–LGb.

The reason is that propane is a relatively large molecule with 11 atoms.

Tables 6 and 7 show the difference in the speed of sound for a mole fraction mxture of 70% methane and 30% carbon dioxide in the real gas region, calculated by models based on isotropic statistical thermodynamics (JZG), nonisotropic models obtained from the perturbation part of the reference LJ potential (JZG–LGa), and models obtained by classical thermodynamics (BWR and BWRSN). In comparison with experimental results,[42] however, somewhat larger deviations can be found in the high-pressure region due to the large influence of the higher-order multipolar, dispersion forces. On the basis of AAD (Table 6), we can conclude that the best results come from the JZG–LGa model.

Because of spherical symmetry, the molecules of methane have no dipole and quadrupole moments. The linear molecules of carbon dioxide, on the other hand, have a relatively very high effect of nonisotropic interactions resulting from the quadrupole moment.[2,3] Nevertheless, the results obtained by means of the JZG model show only about a 2% AAD (Table 6) due to a relatively small mole fraction of carbon dioxide. Table 7 shows ARVS in relation to pressure and temperature. The greatest effect of nonisotropic interactions is found in the low-temperature and high-pressure region, where the contribution of nonisotropic interactions to the speed of sound is even higher than 4%.

Tables 8 and 9 show the variation in the results for ammonia among analytical computations based on statistical thermodynamics (JZG and JZG–LGa), classical thermodynamics (JS, BWR, and BWRSN), and experimental thermodynamic data.[40]

Our expectations concerning a strong influence of nonisotropic interactions for ammonia were realized. Ammonia, as a relatively very polar substance, has a large dipole and quadrupole moments.[2] In the higher pressure regions, above all, the contribution of nonisotropic interactions to the speed of sound may exceed 20% (Fig. 4).

We concentrated of the study of the influence of anisotropic interaction to the speed of sound in the case of real gases. The Lucas–Gubbins (LG) model (JZG–LGa and JZG–LGb) yields better results, especially at high pressures, than the MWF model (JZG–MWF). The advantage of JZG–LG models is that, apart from the influence of multipolar moments, they also take into account the polarization effects. Simultaneously, with the development of the JZG–LG models, the mathematical model dealing with higher orders of multipole moments can be developed, for example, the octopole moment.

As evident from Tables 4–9 and Figs. 3 and 4, the influence of nonisotropic interactions is very important in the region of high pressure or in the region where the compressibility factor deviates sharply from ideality. What is crucial here is the shape of the molecules and their molecular structure.

Summary

The paper presents a mathematical model for computation of the speed of sound in the gaseous regions.

For a real fluid, the JZG model, based on molecular dynamics and LJ simulations and a modified BWR EOS, was applied. Multipolar and induction interactions are calculated with the help of quantum mechanical calculation of the intermolecular energy function, the L–G perturbation theory, and the MWF model. The multipole expansion is terminated at the quadrupole term.

The analytical results are compared with the thermodynamic data and analytical results obtained by classical thermodynamics, and they show very good agreement.

References

[1] Barker, J. A., and Henderson, D., "What is Liquid? Understanding the States of Matter," *Reviews of Modern Physics*, Vol. 48, No. 4, 1976, pp. 587–671.

[2] Gray, C. G., and Gubbins, K. E., "Intermolecular Forces," *Theory of Molecular Fluids*, Clarendon, Oxford, 1984, pp. 27–141.

[3] Lucas, K., "The Ideal Gas, Intermolecular Forces, Perturbation Theory," *Applied Statistical Thermodynamics*, Springer-Verlag, New York, 1992, pp. 97–251, 370–430.

[4] Cotterman, R. L., Schwarz, B. J., and Prausnitz, J. M., "Molecular Thermodynamics for Fluids at Low and High Densities, Part I: Pure Fluids Containing Small or Large Molecules," *AIChE Journal*, Vol. 32, No. 11, 1986, pp. 1787–1798.

[5] Cotterman, R. L., and Prausnitz, J. M., "Molecular Thermodynamics for Fluids at Low and High Densities, Part II: Phase Equilibria for Mixtures Containing Components with Large Differences in Molecular Size or Potential Energy," *AIChE Journal*, Vol. 32, No. 11, 1986, pp. 1799–1811.

[6] Moser, B. J., "Die molekulartheoretische Behandlung von VLE-Berechnungen," *Die Theorie der Intermolekularen Wechselwirkungen und Ihre Anwendung auf die Berechnung von Verdampfungsgleichgewichten binrer Systeme*, Ph.D. Dissertation, Univ. of Duisburg, Duisburg, Germany, 1981, pp. 21–122.

[7] Shukla, K., "Thermodynamic Properties of Binary Mixtures of Atoms and Diatomic Molecules from Computer Simulation and Perturbation Theory," *Fluid Phase Equilibria*, Vol. 127, No. 1–2, 1997, pp. 1–20.

[8] Gubbins, K. E., "Applications of Molecular Simulation," *Fluid Phase Equilibria*, Vol. 83, No. 1, 1993, pp. 1–14.

[9] Calero, S., Wedland, M., and Fischer, J., "Description of Alternative Refrigerants with BACKONE Equations," *Fluid Phase Equilibria*, Vol. 152, No. 1, 1998, pp. 1–22.

[10] Müller, A., Winkelmann, J., and Fischer, J., "Backone Family of Equations of State: 1. Nonpolar and Polar Pure Fluids," *AIChE Journal*, Vol. 42, No. 4, 1996, pp. 1116–1126.

[11] Saeger, B., and Fischer, J., "Construction and Application of Physically Based Equations of State, Part II: The Dipolar and Quadrupolar Contributions to the Helmholtz Energy," *Fluid Phase Equilibria*, Vol. 72, No. 1, 1992, pp. 67–88.

[12] Saeger, B., and Fischer, J., "Construction and Application of Physically Based Equations of State, Part III: Correlative and Predictive Application to the Refrigerants R22," *Fluid Phase Equilibria*, Vol. 93, No. 1, 1994, pp. 101–140.

[13] Shukla, K., "Phase Equilibria and Thermodynamic Properties of Molecular Fluids from Perturbation Theory," *Fluid Phase Equilibria*, Vol. 96, No. 1, 1994, pp. 19–49.

[14] Luckas, M., Lucas, L., Deiters, U., and Gubbins, K. E., "Integrals over Pair- and Triplet-Correlation Functions for the Lennard-Jones (12-6) Fluid," *Molecular Physics*, Vol. 57, No. 2, 1986, pp. 241–253.

[15] Guevara, Y., Benavides, A. L., and del Rio, F., "Thermodynamics of a Square-Well Octopolar Fluid," *Molecular Physics*, Vol. 89, No. 5, pp. 1277–1290.

[16] Strogyn, D. E., "Third Virial Coefficients of Nonspherical Molecules," *Journal of Chemical Physics*, Vol. 30 , No. 11, 1969, pp. 4269–4986.

[17] Rowlinson, J. S., "The Third Virial Coefficients of Polar Gases," *Journal of Chemical Physics*, Vol. 19, No. 7, 1951, pp. 827–831.

[18] Rowlinson, J. S., "The Critical Constants of Polar Gases," *Journal of Chemical Physics*, Vol. 19, No. 7, 1951, pp. 831–837.

[19] Ameling, W., Shukla, K. P., and Lucas, K., "Third Virial Coefficient of Simple Linear Molecules," *Molecular Physics*, Vol. 58, No. 2, 1986, pp. 381–394.

[20] Lee M.-J., and Chen, J.-T, "An Improved Model of Second Virial Coefficients of Polar Fluids and Fluid Mixtures," *Journal of Chemical Engineering of Japan*, Vol. 31, No. 4, 1998, pp. 518–526.

[21] Hirschfelder, O. O., Curtiss, C. F., and Bird, R. B., "The Equation of State of Gases at Low and Moderate Densities," *Molecular Theory of Gases and Liquids*, Wiley, London, 1954, pp. 131–230.

[22] Heinemann, D., Ripke, M., and Lucas, K., "Thermodynamic Properties of Fluid Oxygen from the SSR-MPA Potential," *Fluid Phase Equilibria*, Vol. 86, No. 1, 1993, pp. 15–25.

[23] Sediawan, W. B., Gupta, S., and McLaughin, E., "Computer Modelling of Naphtalene," *Journal of Chemical Physics*, Vol. 90, No. 3, 1989, pp. 1888–1900.

[24] Twu, C., and Gubbins, K. E., "Thermodynamic of Polyatomic Fluid Mixtures, Part II: Polar Quadrupolar and Octopolar Molecules," *Chemical Engineering Science*, Vol. 33, 1978, pp. 879–887.

[25] Münster, A., "Volume I: General Foundations, Theory of Gases," *Statistical Thermodynamics*, Springer-Verlag, New York, 1960, pp. 3–242.

[26] Smirnova, N. A., "Classical Statistics of Ideal Gas, Real Gases, Intermolecular Forces," *Methods of the Statistical Thermodynamics in the Physical Chemistry*, Univ. of Moscow, Moscow, 1982, pp. 87–113, 270–310.

[27] McClelland, B. J., "The Canonical Ensemble," *Statistical Thermodynamics*, Chapman and Hall, London, 1980, pp. 299–321.

[28] Bosnjakovic, F., "Part Two: Speed of Sound," *Thermodynamics*, Tehnicka Knjiga, Zagreb, Croatia, 1976, pp. 57–60.

[29] Margenau, H., and Kestner, N. R., "Forces Between Molecules," *Theory of Intermolecular Forces*, Pergamon, Oxford, 1969, pp. 222–263.

[30] Rigby, M., Smith, E. B., Wakeham, W. A., and Maithland, G. C., "The Nature of Intermolecular Forces," *The Forces Between Molecules*, Clarendon, Oxford, 1986, pp. 1–35.

[31] Nicolas, J. J., Gubbins, K. E., Street, W. B., and Tildesley, D. J., "Equation of State for Lennard–Jones Fluid," *Molecular Physics*, Vol. 37, No. 5, 1979, pp. 1429–1454.

[32] Adachi, Y., "Generalized Equation of State for Lennard–Jones Fluids–I. Pure Fluids and Simple Mixtures," *Fluid Phase Equilibria*, Vol. 39, No. 1, 1988, pp. 1–38.

[33] Miyano, Y., "An Equation of State for Lennard–Jones Pure Fluids Applicable over a Very Wide Temperature Range," *Fluid Phase Equilibria*, Vol. 85, No. 1, 1993, pp. 71–80.

[34] Johnson, J. K., Zollweg, J. A., and Gubbins, K. E., "The Lennard–Jones Equation of State Revisited," *Molecular Physics*, Vol. 78, No. 3, 1993, pp. 591–618.

[35] Gubbins, K. E., and Twu, C. H., "Thermodynamics of Polyatomic Fluid Mixtures," *Chemical Engineering Science*, Vol. 33, 1978, pp. 863–878.

[36] Jacobsen, R. T., Stewart, R. B., Jahangiri, M., and Pononcello, S., "A New Fundamental Equation for Thermodynamic Property Correlations," *Advances in Cryogenic Engineering*, Vol. 31, Plenum, New York, 1986, pp. 1161–1169.

[37] Walas, S. M., "Equations of State," *Phase Equilibria in Chemical Engineering*, Butterworths, Boston, 1984, pp. 1–110.

[38] Nishiumi, H., and Saito, S., "An Improved Generalized BWR Equation of State Applicable to Low Reduced Temperatures," *Journal of Chemical Engineering of Japan*, Vol. 8, No. 5, 1975, pp. 356–361.

[39] Nishiumi, H., "An Improved Generalized BWR Equation of State Applicable to Polar Substances," *Journal of Chemical Engineering of Japan*, Vol. 13, No. 3, 1980, pp. 178–183.

[40] Petrak, J., and Ludek, L., "R 290, R 717," *Thermokinetic Properties of Refrigerants*, Faculty of Mechanical Engineering, Consulting and Instructing Center, the Dept. of Compressors, Refrigeration and Hydraulic Machines, Faculty of Mechanical Engineering, Czech Technical Univ., Prague, 1993, pp. 106–109, 120–129.

[41] Rowlinson, J. S., and Swinton, F. L., "The Thermodynamic Properties," *Liquids and Liquid Mixtures*, Butterworths, London, 1981, pp. 11–51.

[42] Younglove, B. A., Frederick, N. V., and McCarthy, R. D., "Experimental Speed of Sound for the Binary Mixture Methane 0.7-Carbon Dioxide 0.3," *Speed of Sound Data and Related Models for Mixtures of Natural Gas Constituents*, National Inst. of Standards and Technology, NIST Monograph 178, Washington, DC, 1993, p. 62.