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Calculation of the Speed of Sound and Other Thermophysical Properties

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

A mathematical model is featured for computing the velocity of sound and other thermophysical properties in the liquid, the gas, and the two-phase domains with the help of statistical thermodynamics. All important contributions (translation, rotation, internal rotation, vibration, intermolecular potential energy, and influences of electron and nuclei excitation) are included. To calculate the thermodynamic properties of real gases, we develop the cluster theory, which yields better results than the virial equation. For the realm of real liquids, the Johnson–Zollweg–Gubbins model (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) based on the modified Benedict–Webb–Rubin equation was applied. The Lennard–Jones inermolecular potential was used. The analytical results are compared with the experimental data and models obtained by classical thermodynamics and show relatively good agreement.

Nomenclature

A = free energy
C_p = molar heat capacity at constant pressure
C_V = molar heat capacity at constant volume
c_p = specific heat capacity at constant pressure
c_0 = velocity of sound
E = potential energy
f = Mayer function
G = free enthalpy
g = degeneration number
H = enthalpy, Hamiltonian
$h, \hbar$ = Planck constant
I_1, I_2, I_1^* = integrals
k = Boltzmann constant
N = number of molecules in system
N_1 = number of molecules in cluster
p = pressure, momentum
S = entropy
T = temperature
U = internal energy
V = volume
v = specific volume
Z = partition function
ε = Lennard–Jones parameter
θ = characteristic temperature
μ = chemical potential
ρ = density
σ = Lennard–Jones parameter, symmetric number
Ψ = wave function

Superscripts and Subscripts

conf = configuration
el = influence of electron excitation
ir = internal rotation
nuc = influence of nuclear excitation
pot = potential energy
rot = rotation
trans = translation
vib = vibration
0 = ground state

Introduction

THIS paper presents a mathematical model for computing the speed of sound and other thermophysical properties using statistical thermodynamics. For real gases, we developed a cluster theory, based on the principle of average clusters, which yields better results than the virial equation. For real liquids, the Johnson–Zollweg–Gubbins (JZG)[1] model, based on the modified Benedict–Webb–Rubin (BWR) equation[1] and a great number of Monte Carlo and molecular dynamics simulations, was applied.

The results of the analysis are compared with experimental data and show relatively good agreement, especially for real gases. Somewhat larger deviations, however, can be found in the real liquid region due to the large influence of the attraction and repulsion forces because the Lennard–Jones potential is an approximation of the actual real intermolecular potential.

Computation of Thermodynamic Properties of the State

Let us consider the system of N equal molecules of real gas or of real liquid. Molecules move either individually or in small instantaneous clusters.[2] The size and shape of the cluster changes due to the existence of intermolecular and intramolecular interactions between electrons and nuclei in the system. The energy in such a molecules system consists of the kinetic energy of the molecules and the atoms, the intermolecular potential energy, the energy of the electrons as to the energy level they belong to, and the energy of the nuclei as to the energy level they belong to.

To obtain an accurate calculation it is necessary to solve the Schrödinger equation for several particles[3]:

$$\left(-\sum_{i}\frac{\hbar^2}{2m_i}\nabla_i^2+\sum_{i<j}\frac{q_iq_j}{r_{ij}^2}\right)\psi=\frac{\hbar}{i}\frac{\partial\psi}{\partial t} \tag{1}$$

where the sums are taken over all nuclei and electrons with appropriate masses m_i and charges q_i.

Any solution of such a differential equation is a difficult task, although reasonably accurate results can be obtained using the following generalizations: 1) Intermolecular forces are much weaker

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[*] Mechanical Engineer, P.O. Box 224, Department of Thermodynamics, Faculty of Mechanical Engineering, Smetanova 17; jurij.avsec@uni-mb.si. Member AIAA.

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

than intramolecular forces; therefore, both intramolecular forces and intermolecular forces can be treated quite independently. 2) Intermolecular potential energy depends only on the position of the nuclei in space. 3) The effect of the orientation of the molecule in space has been neglected. 4) It is assumed that intermolecular potential is additive. 5) Each of the modes of motion is independent of the others.

In spite of the five mentioned simplifications, solving the many-body Schrödinger equation (1) still constitutes a very hard task, and so we apply classical statistical thermodynamics to computate the thermodynamic functions of state. To calculate the thermodynamic functions of state we apply the canonical partition.[4] The semiclassical formulation of the canonical ensemble for N indistinguishable molecules can be expressed as follows:

$$Z = \frac{1}{N!h^{Nf}} \times \int \cdots \int \exp\left(-\frac{H}{kT}\right) \cdot \mathrm{d}r_1\,\mathrm{d}r_2, \ldots, \mathrm{d}r_N\,\mathrm{d}p_1\,\mathrm{d}p_2, \ldots, \mathrm{d}p_N \tag{2}$$

where f is the number of degrees of freedom of the individual molecule and H the Hamiltonian molecule system. With the help of the canonical ensemble for the system of N molecules, the partition function can be expressed as

$$Z = Z_0 Z_{\mathrm{trans}} Z_{\mathrm{vib}} Z_{\mathrm{rot}} Z_{\mathrm{ir}} Z_{\mathrm{el}} Z_{\mathrm{nuc}} Z_{\mathrm{conf}} \tag{3}$$

Thus, the partition function Z is a product of the terms of the ground state 0, the translation trans, the vibration vib, the rotation rot, the internal rotation ir, the influence of electrons excitation el, the influence of nuclei excitation nuc, and the influence of the intermolecular potential energy conf.

The canonical theory for computating the thermodynamic functions of the state can expressed as follows.[5,6]

Pressure:

$$p = kT\left(\frac{\partial \ln Z}{\partial V}\right)_T \tag{4a}$$

Internal energy:

$$U = kT^2\left(\frac{\partial \ln Z}{\partial T}\right)_V \tag{4b}$$

Entropy:

$$S = k\left[\ln Z + T\left(\frac{\partial \ln Z}{\partial T}\right)_V\right] \tag{4c}$$

Enthalpy:

$$H = kT\left[T\left(\frac{\partial \ln Z}{\partial T}\right)_V + V\left(\frac{\partial \ln Z}{\partial V}\right)_T\right] \tag{4d}$$

Free enthalpy:

$$G = -kT\left[\ln Z - V\left(\frac{\partial \ln Z}{\partial T}\right)_V\right] \tag{4e}$$

The computation of the individual terms of the partition function and their derivatives are dealt with in the works of Lucas,[4] Gray and Gubbins,[6] and McClelland.[7] Table 1 shows the individual terms of the partition function with the exception of the configurational integral.

Table 1 Calculation of the single terms of the partition function

Form	Partition function
Translation	$Z = V^N\left[\frac{2\cdot\pi\cdot m\cdot k\cdot T}{h^2}\right]^{3\cdot N/2}$
Two-atom heteronuclear molecule	$1 \geq 1.4C : Z = \left(\frac{1}{C}\right)^N\left(1 + \frac{C}{3} + \frac{C^2}{15} + \frac{4C^3}{315}\right)^N$ $1 < 1.4C : Z = [1 + 3\exp(-2C) + 5\exp(-6C)\cdots]^N$ $C = \theta_{\mathrm{rot}}/T$
Two-atom homonuclear molecule	$1 \geq 0.3C : Z = \frac{1}{2}\left[\frac{1}{C}\right]^N\left(1 + \frac{C}{3} + \frac{C^2}{15} + \frac{4C^3}{315}\right)^N$ $1 < 0.3C : Z = f(Z_{\mathrm{orto}}, Z_{\mathrm{para}})$
Linear polyatomic molecule	$Z = [8\pi^2 IkT/\sigma h^2]^N$
Non-linear polyatomic molecule	$Z = [8\pi^2 kT/\sigma h^2]^N(\pi I_A I_B I_C)^{N/2}$
Vibration of atoms in molecule	$Z = \left(\prod_i^p\left\{1/\left[1 - \exp(-\theta_{\mathrm{vib}_i}/T)\right]\right\}\right)$
Influence of electrons excitations	$Z = \{g_{\mathrm{el}(0)} + g_{\mathrm{el}(1)}\exp[-(\theta_{\mathrm{el}}/T)]\}^N$
Influence of nuclei excitations	$Z = g_{\mathrm{nuc}(0)}^N$
Internal rotation	$u_{\mathrm{ir}_{\max}}/kT \gg 10$: normal vibration $u_{\mathrm{ir}_{\max}}/kT \approx 0 : Z = 1/\sigma_{\mathrm{ir}}^N\left[8\pi^2 I_{\mathrm{ir}}kT/h^2\right]^{N/2}$ $0 < u_{\mathrm{ir}_{\max}}/kT < 10$: Pitzer tables

Velocity of Sound

Velocity of sound refers to the velocity of the mechanical longitudinal pressure waves propagation through a medium. It is an important parameter in the study of compressible flow. The calculation of the speed of sound is very important in measurement (acoustic resonance level gauge[8]). The propagation of sonic waves for real fluids is in almost all cases nearly isentropic.[9,10] Therefore, we can calculate the isentropic speed of sound for real fluids as

$$c_0 = \sqrt{-v^2\left(\frac{\partial p}{\partial v}\right)_s} \tag{5}$$

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

$$\begin{aligned}
\mathrm{d}s &= \frac{c_p}{T}\cdot\mathrm{d}T - \left(\frac{\partial v}{\partial T}\right)_p\cdot\mathrm{d}p = 0\\
&= \frac{c_p}{T}\cdot\left[\left(\frac{\partial T}{\partial v}\right)_p\cdot\mathrm{d}v + \left(\frac{\partial T}{\partial v}\right)_v\cdot\mathrm{d}p\right] - \left(\frac{\partial v}{\partial T}\right)_p\cdot\mathrm{d}p = 0\\
&\rightarrow \left(\frac{\partial p}{\partial v}\right)_s = \frac{c_p}{T}\left(\frac{\partial T}{\partial v}\right)_p \bigg/ \left[\left(\frac{\partial v}{\partial T}\right)_p - \frac{c_p}{T}\left(\frac{\partial T}{\partial p}\right)_v\right]
\end{aligned}$$

$$c_0 = \sqrt{-v^2\left\{\frac{c_p}{T}\left(\frac{\partial T}{\partial v}\right)_p \bigg/ \left[\left(\frac{\partial v}{\partial T}\right)_p - \frac{c_p}{T}\left(\frac{\partial T}{\partial p}\right)_v\right]\right\}} \tag{6}$$

Therefore, the velocity of sound is a function of the thermodynamic properties of the fluid.

Configurational Integral

We focus on the computation of thermodynamic properties of the Lennard–Jones fluid. The calculus of the configuration integral is being developed in some major directions.[3–5,11–13] For several decades, less complex mathematical models have appeared, obtained through statistics, although their applicative value is very limited (primarily for computations in the diluted gas region). Semitheoretical models, on the other hand, have found a much wider application, in particular, for mixtures. In spite of much more accurate results when compared with the simpler models, their application in practical calculations is still questionable. The advantage of semitheoretical models lies in their relative simplicity. The development of integral equations is very important. Comparison of the results obtained using semitheoretical models with experimental results shows that matching is good only in the region of lower densities. Today, by the use of integral equations, some simple systems are resolved, such as the hard spheres system. Thus far, numerous attempts for the use of analytical derivation of integral equations for more complex potentials have been unsuccessful. Nevertheless, analytically resolved models using integral equations are very important for additional calculus in other theories, primarily the perturbation theories. Currently, the perturbation models are frequently used. To calculate thermal quantities in real fluids, expansion theories are of utmost importance. For the region of real gases, the method of classical virial expansion has become established. In real fluids, though, the model of expansion of probability densities is used.

To compare the accuracy of analytical models, we often use numerical methods. The Monte Carlo method and the method of molecular dynamics have found to be particularly good applications. Neither method is suitable for practical use because they require too much computer time. By the use of the modified thermal equations and approximation procedures, the results of numerical methods may be used to define the coefficients in equations. This is especially important for determining the coefficients of the Lennard–Jones fluid.

In real gas, there are relatively weak intermolecular forces. The real gas molecules move either individually or in small instantaneous and random clusters. To solve the configurational integral, we devised a method of clusters.[2] The method is based on the principle of average clusters.

An average cluster of N_1 molecules can be determined by dealing with a sufficiently large number N of molecules in the system. Figure 1 demonstrates the method of clusters showing the activity of the intermolecular forces in clusters, as well as the activity of intermolecular forces between clusters.

Analysis of the motion of the molecules by the Monte Carlo method[14] indicates that the number of molecules in the average cluster is relatively low. The number of molecules in the average cluster depends on the average intermolecular distance.

Thus, the ideal gas can, for example, have one molecule in any of the clusters that are dispersed at such distances that the intermolecular forces are negligible.

The principal idea of the method of clusters stipulates that the intermolecular potential energy of the system can be split into the intermolecular potential energy in clusters, $E_{\mathrm{pot}\,1}$, and the intercluster potential energy due to interactions between clusters, $E_{\mathrm{pot}\,2}$. Therefore, the potential intermolecular energy can be written as the sum of both parts:

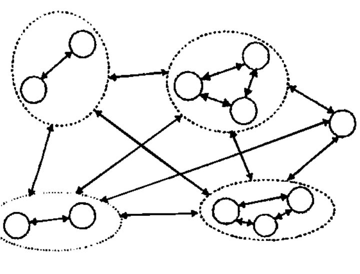

Fig. 1 Schematic outline of clusters.

$$E_{\mathrm{pot}} = E_{\mathrm{pot}\,1} + E_{\mathrm{pot}\,2} \tag{7}$$

Based on the suppositions of the preceding section, the configurational integral can then be expressed as follows:

$$Z_{\mathrm{conf}} = Z_{\mathrm{conf}\,1} + Z_{\mathrm{conf}\,2} \tag{8}$$

When computing the configurational integral $Z_{\mathrm{conf}\,1}$, the effects of mutual interactions of up to three molecules in the cluster were taken into account. For the intermolecular potential, the Lennard–Jones potential was applied. The configurational integral $Z_{\mathrm{conf}\,1}$ that takes interactions in clusters into account can be written[7,11,12] as

$$\begin{aligned} Z_{\mathrm{conf1}} = \left(\frac{1}{V_1}\right)^N \Bigg[& \int_{V_1} \cdots \int_{V_1} \mathrm{d}r_1, \ldots, \mathrm{d}r_{N_1} \\ & + \int_{V_1} \cdots \int_{V_1} \sum f_{ij}\, \mathrm{d}r_1, \ldots, \mathrm{d}r_{N_1} \\ & + \int_{V_1} \cdots \int_{V_1} \sum (f_{ij} f_{kl})\, \mathrm{d}r_1, \ldots, \mathrm{d}r_{N_1} + \cdots \Bigg]^{N/N_1} \end{aligned} \tag{9}$$

$$V_1 = (N_1/N)V \tag{10}$$

Equation (9) can also be expressed as[5]

$$\begin{aligned} \ln Z_{\mathrm{conf}\,1} = \frac{N}{N_1} \cdot \ln \Bigg\{ \Bigg[& 1 + \frac{(N_1 - 1)N I_1}{2V} \\ & + N^2 \left(1 - \frac{1}{N_1}\right)(N_1 - 2) I_2 \Bigg] \Big/ \; 6V^2 \Bigg\} \end{aligned} \tag{11}$$

$$I_1 = \frac{1}{V_1} \cdot \int \int f_{ij} \cdot \mathrm{d}r_1\, \mathrm{d}r_2$$

$$I_2 = \frac{1}{V_1} \int \int \int [3 f_{ij} \cdot f_{kl} + f_{ij} \cdot f_{kl} \cdot f_{mn}] \cdot \mathrm{d}r_1\, \mathrm{d}r_2\, \mathrm{d}r_3 \tag{12}$$

where f is the Mayer function.[6]

The integral I_1 for the Lennard–Jones potential case is solved by Reichl[13] and Hirschfelder et al.[12] The integral I_2 was transformed by Mönster[11] as follows:

$$I_2 = 3I_1^2 + I_{21}, \qquad I_{21} = \frac{N_1}{V} \int \int \int f_{ij} \cdot f_{kl} \cdot f_{mn} \cdot \mathrm{d}r_1\, \mathrm{d}r_2\, \mathrm{d}r_3 \tag{13}$$

The integral I_{21} is resolved in the works of Reichl[13] and Hirschfelder et al.[12] for the Lennard–Jones potential case.

The effect of intercluster interaction can be presented by the configurational integral $Z_{\mathrm{conf}\,2}$, which takes the mutual interactions of two clusters in the system:

$$Z_{\mathrm{conf}\,2} = \frac{1}{V^{N/N_1}} \int \int \cdots \int \exp\left(-\frac{U_{ij}}{kT}\right) \mathrm{d}r_1\, \mathrm{d}r_2, \ldots, \mathrm{d}r_{N/N_1} \tag{14}$$

where U_{ij} is the potential energy between the i and j clusters. Applying the method in Ref. 12 to the diluted systems case, we have

$$U_{ij} = N_1^2 u_{ij} \tag{15}$$

where u_{ij} is the potential energy between the molecule in cluster i and the molecule in cluster j.

Utilizing Eq. (15) and taking only the mutual interaction of two clusters in the system, we can write

$$F_{ij} = \exp\left(-\frac{U_{ij}}{kT}\right) - 1, \qquad I_1^* = \frac{1}{V} \int \int F_{ij} \cdot \mathrm{d}r_1\, \mathrm{d}r_2$$

$$N_2 \approx \frac{N}{N_1} \tag{16}$$

Table 2 Coefficients for MBWR equation of state

i	a_i	b_i	G_i
1	$x_1 T^* + x_2 \sqrt{T^*} + x_3 + x_4 / T^* + x_5 / T^{*2}$	$x_{20} / T^{*2} + x_{21} / T^{*3}$	$(1 - F)/(2\gamma)$
2	$x_6 T^* + x_7 + x_8 / T^* + x_9 / T^{*2}$	$x_{22} / T^{*2} + x_{23} / T^{*4}$	$-(F\rho^{*2} - 2G_1)/(2\gamma)$
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	$x_{17} / T^* + x_{18} / T^*$	——	——
8	x_{19} / T^{*2}	——	——

Table 3 Saturated pressure for ethane

	P, bar			
T, K	CT	ST	JZG	Exp.
153	0.127	0.126	0.127	0.127
173	0.524	0.524	0.527	0.526
193	1.58	1.58	1.59	1.58
213	3.79	3.76	3.88	3.82
233	7.80	7.66	7.67	7.83
253	14.3	13.83	13.88	14.32
263	18.2	17.49	17.62	18.65
273	24.0	22.7	22.95	23.94
283	30.5	28.2	28.6	30.28
293	38.0	33.9	34.8	37.86
301	44.8	——	——	44.9
AAD	0.0054	0.041	0.034	——

where N_2 and F_{ij} are the number of clusters in the system and Mayer's function. Integral I_1^* can be solved in the same way as I_1:

$$\ln Z_{\text{conf}\,2} = +(N_2^2 / 2V) I_1^* \tag{17}$$

To determine the number of molecules in an average cluster and the number of clusters of a real gas, we take advantage of the experimental results of the thermodynamic functions of the state obtained by results[14] of a simulation using the Monte Carlo method. After an thorough analysis, the number of molecules in a individual average cluster was established: $1 < N_1 < 6$.

In the higher pressure and low density region, perturbation methods or models obtained by numerical simulations (Monte Carlo, molecular dynamics) are employed. For a real liquid, the JZG model,[1] based on molecular dynamics and Monte Carlo simulations with the Lennard–Jones intermolecular potential and modified BWR (MBWR) equation of state, was used (see Table 2). Thus, we can express configurational free energy A_{conf} as

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

$$\rho^* = N\sigma^3 / V, \qquad T^* = kT/\varepsilon, \qquad A^*_{\text{conf}} = A_{\text{conf}} / N\varepsilon$$

$$F = \exp(-\gamma \rho^{*2}), \qquad \gamma = 3 \tag{19}$$

Equation (18) accurately correlates thermophysical properties from the triple point to about 4–5 times the critical temperature. In Eq. (18), there are x_j adjustable parameters in the equation of state.

The constants necessary for the computation, such as the characteristic rotation, vibration, electronic, etc., temperatures, are obtained from experimental data.[15–19] The inertia moments are obtained analytically by applying knowledge of the atomic structure of the molecule. Constants for the Lennard–Jones potential are obtained from the literature.[4,5,12]

We also carried out calculations for methane (CH_4), difluorodichloromethane (CF_2Cl_2), ammonia (NH_3), ethane (C_2H_6), and argon (Ar). Comparison of our calculations with experimental results by Maxwell,[15] Edmister and Lee,[16] Eckert and Drake,[20] Petrak and Ludek,[21] Younglove et al.,[10] Borgnakke and Sonntag,[22] Ermakova et al.,[23] and Gammon and Douslin[24] are presented in Tables 3–7.

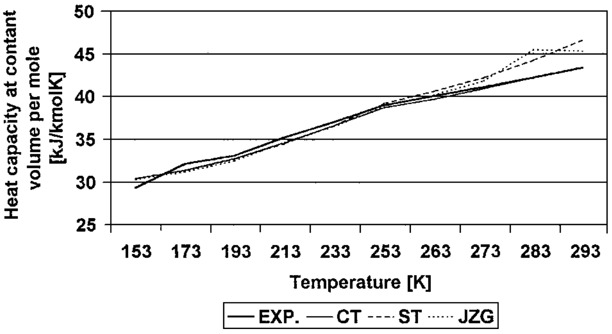

Fig. 2 Heat capacity at constant volume per mole for ethane in the region of saturated vapor.

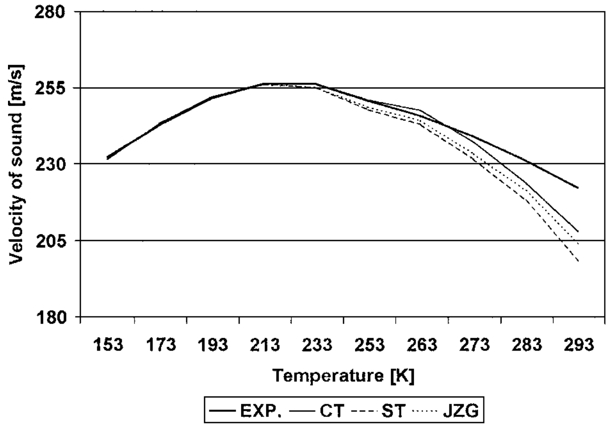

Fig. 3 Velocity of sound for ethane in the region of saturated vapor.

Figures 2 and 3 and Table 3 show the deviation of the results for ethane in the saturated gas region. Table 4 shows the deviation of the results for CF_2Cl_2 for the real gas region between the analytical computation and the experimental values. The results show relatively good agreement. Table 5 shows the deviation of the results for ammonia between the analytical computation with help of statistical thermodynamics [cluster theory (CT) and statistical theory (ST) with the help of classical virial expansion,[11,25] JZG model] and models obtained by classical thermodynamics. Today, there are numerous equations of state (EOS) reported in the literature for describing the behaviors of fluid with help of classical thermodynamics, for example, Van der Waals EOS (VDW)[26] and Peng-Robinson (PR).[26] However, these equations have exhibited some noticeable defects, such as poor agreement with experimental data at moderate densities. However, we can use the complex EOS with many constants [BWR EOS (see Ref. 26), BWR–Starling–Nishiumi EOS (BWRSN) (see

Table 4 Comparison between analytical calculation and experimental data for difluordichlormethane in the region of superheated vapor

		10 bar			20 bar		
T, K	Method	V, m^3/kmol	H, kJ/kmol	S, kJ/kmol·K	V, m^3/kmol	H, kJ/kmol	S, kJ/kmol·K
373	JZG	2.81	29,120	97.1	1.25	28,440	91.0
373	ST	2.80	29,060	98.5	1.25	28,270	91.1
373	CT	2.80	29,990	97.9	1.22	28,280	89.2
373	Exp	2.79	29,936	97.9	1.21	28,646	89.6
423	JZG	3.30	36,900	106.1	1.55	35,380	105.4
423	ST	3.30	33,190	109.0	1.55	32,560	102.2
423	CT	3.29	34,880	109.3	1.56	33,950	102.4
423	Exp	3.29	34,637	109.1	1.53	33,358	101.8
473	JZG	——	——	——	1.82	40,840	114.1
473	ST	——	——	——	1.80	36,950	111.1
473	CT	——	——	——	1.82	38,760	109.3
473	Exp	——	——	——	1.79	38,274	104.5

Table 5 Velocity of sound for NH_3 in comparison with experimental data[20–22]

	C_0, m/s							
T, K	VDW	PR	BWRSN	JS	JZG	CT	ST	Exp.
223	376	376	375	377	377	377	377	376
243	391	389	389	389	390	390	390	389
263	403	401	401	398	400	401	399	399
283	412	409	410	403	405	408	404	406
303	417	413	414	404	403	412	401	410
323	416	413	414	401	392	411	389	409
343	427	409	427	393	369	405	363	402
363	389	403	398	379	323	390	310	388
373	374	399	390	369	——	378	——	377
AAD	0.014	0.016	0.018	0.012	0.035	0.004	0.047	——

Table 6 Comparison between the analytical calculation (JZG) and the experimental data for argon (R-740) in the region of compressed liquid

	C_v, kJ/kmol·K		C_p, kJ/kmol·K		P, bar		C_0, m/s	
T, K	JZG	Exp.	JZG	Exp.	JZG	Exp.	JZG	Exp.
110	17.7	18.9	43.3	45.6	4.65	4.5	678	701
200	17.1	17.8	32.1	34.5	110	100	804	851
300	13.3	13.8	28.0	30.5	22	20	386	371
300	14.3	14.9	29.1	32.4	63	60	574	570
300	15.1	15.7	29.4	31.0	110	100	716	731
400	14.1	14.6	26.3	26.8	106	100	685	689
500	13.6	14.1	24.9	26.4	105	100	685	683
600	14.6	13.7	23.4	25.0	110	100	755	731
AAD	0.044	——	0.061	——	0.061	——	0.024	——

Refs. 26–28), and Jacobsen–Stewart EOS (JS) (see Refs. 29 and 30)]. These equations are more complicated, but they have no insight into the microstructure of matter and there is poor agreement with experimental data outside the interpolation limits. The calculation of the thermodynamical functions of state with help of classical thermodynamics is well known[9,31] and is not described here. The effects of mutual interactions of up to three molecules in the cluster were taken into account using the procedure of computing the configurational integral with the help of statistical thermodynamics based on classical virial expansion (ST).

With real gases (Figs. 2 and 3 and Tables 3–5), the results are equally good. The CT yields better results, especially at high pressures, than the classical statistical virial form of the EOS (ST). The average absolute deviation (AAD) was obtained by

$$\sum |(\text{data}_{\text{exp}} - \text{data}_{\text{calc}})/\text{data}_{\text{exp}}|/\text{no. of points}$$

As shown in the last row of Tables 3 and 5, the AAD clearly indicates that our CT is an improvement over the classical virial expansion theory. The improvement is more impressive in the high-pressure region.

Table 7 Velocity of sound for R50 in the liquid region

		JS[a]	JZG[b]	Exp.[21,24]
T, K	V, m^3/kmol	C_0, m/s	C_0, m/s	C_0, m/s
100	0.0365	1452	1525	1443
120	0.0391	1257	1302	1250
140	0.0425	1043	1117	1039
160	0.0476	801	900	789
180	0.0581	497	601	494

[a] AAD = 0.09. [b] AAD = 0.127.

However, somewhat larger deviations are found in the region of real liquid (Tables 6 and 7) due to the large influence of the attraction forces because the Lennard–Jones potential is only an approximation of the actual real intermolecular potential. The discrepancies between the calculated and measured results are higher for methane due to the stronger impact of the polarity of molecules.

Conclusion

The paper presents a mathematical model for the computation of the thermodynamical functions of the state in the liquid, gaseous, and two-phase regions.

For the region of real gases, we developed the method of clusters, based on the average cluster with N_1 molecules in the system with N molecules. The advantage of this method is in the computation of the thermodynamic functions at high pressures. For the real liquid, the JZG model, based on molecular dynamics and Monte Carlo simulations and the modified BWR equation of state, was applied.

The analytical results are compared with the experimental data and analytical calculation obtained by classical thermodynamics and show relatively good agreement.

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