Monomer Fraction in Real Gases

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Abstract

This work is aimed to attract attention to monomer fraction density (MFD), the variable that has not yet taken its place in the theory of real gases. The work shows that this variable can be calculated for monocomponent real gases from experimental isothermal dependences of their density on pressure and can be used for calculations of Gibbs energy, entropy and clusters equilibrium constants in real gases. The MFD-based joint series expansions method for density and pressure is suggested as an alternative to virial expansions. This method corresponds to the chemical equilibrium theory and provides new non-obvious results.

Keywords: Real gas, supercritical fluid, cluster, entropy, virial expansion, equilibrium constant

1. Introduction

The contemporary level of knowledge of interatomic or intermolecular interaction mechanisms does not provide in a full scale and effective enough utilization of microscopic approaches, such as the molecular dynamics methods, for precise calculation of the real gases thermophysical properties starting from the first principles. It is necessary to note that when the accepted level of precision is around 1%, the thermophysical properties of real systems may be described by many different theoretical models. But the precision of the contemporary experimental results is at the level of 10^{-3} %. To provide correlation between theory and experiment at this level of precision, a quite new state of the theoretical knowledge is required.

There is a problem of correlation between theoretical estimations of materials properties, based on the traditional first principles, and empirical equations, put into the basis of modern technology. For example, Reid et al. (1977) points out that for any thermodynamic property (of the same substance) it is necessary to select its own pair of the link energy and the particle diameter entering the Lennard-Jones potential. A growing requirement to have precision of the technological processes control, however, does not permit relying on empirical equations and forces looking critically at the 'first principles' currently used.

For substances, like water, with a polar interaction mechanism, which can be defined with rather good precision, the molecular dynamics (MD) methods give satisfactory results, as is stated in the works of Paricaud et al. (2005; 2007). But currently used assumptions on the type and parameters of the van der Waals forces are more approximate and do not match the current precision of experimental data.

One more problem is connected with a precise determination of the number of states in a multi-particle system. A general opinion, spread in thermodynamics literature, that the so-called 'excluded volume' in monatomic real gases equals four own volumes of atoms, corresponds neither to the experiment nor to the MD simulation results. For example, the graphical results for the MD computation of the hard sphere model, performed by Hoover (1991, Figure 6.1), show that the excluded volume to the own volume ratio does not exceed 1.4.

To move forward in augmenting the effectiveness of theory in material science and technology, it is necessary to improve the methods of the interaction mechanisms' parameters computation from constantly updated experimental data. As an additional and efficient tool for the computational analysis of real gases, this paper suggests use of monomer fraction density (MFD).

The paper develops ideas reported by the author to the Joint European Thermodynamics Conference, JETC IX, Saint Etienne, France,

(Sedunov, 2007a). Its aim is to describe a new thermodynamic approach to real gases. This approach joins in one picture the pressure P, density D, volume V, internal energy E, Gibbs energy G, entropy S basing it on a very important variable – MFD.

The approach is phenomenological and avoids assumptions about intermolecular interactions, but leads to fundamental results that help to interpret and practically use experimental data. One of its goals is to develop the methods of computational analysis of experimental thermophysical data for real gases capable to throw more light on mechanisms of intermolecular interactions in real gases.

2. Physical and Virtual Cluster Fractions in Real Gas and Virial Expansions

A monocomponent real gas consists of uniform basic particles (molecules or atoms), some of them being aggregated temporarily in compact groups (clusters) with different numbers k of basic particles: monomers, dimers, trimers and larger clusters. In this work all extensive values are presented for a mole of basic particles, independent of a status of their aggregations.

2.1 Virial expansions and their physical interpretation

Historically clusters in real gases have been introduced to interpret the results of virial expansions of P (D) or D (P). Feynman (1972) wrote that in the theory of virial expansions it is supposed that the k-order virial coefficient is determined by interactions inside the k-particle group (cluster). He introduced special diagrams to reflect different isomers of clusters with the same number of particles.

Virial expansions play an important role in modern science and technology. For many substances they provide precise enough equations of state (EOS) if based on precise experimental data. But from a theoretical point of view they do not match the chemical equilibrium theory at full length (Sedunov, 2007b). The total density of a real gas, D, entering the virial expansions D (P) or P (D) is the sum of cluster fractions densities, and the total pressure, P, is the sum of partial pressures, P_k. Thus, the virial expansions, operating with total values, instead of partial pressures or partial densities of fractions in a real gas, cannot provide a detailed correlation with the interactions inside the clusters. Feynman (1972) pointed out that the formal program (of the P (V) calculation in all range of the real gas densities) has turned out to be practically unrealizable.

As a mathematical procedure, the virial expansions quite correctly describe empirical correlations between total pressure and total density of real gases. But to investigate the particles interaction mechanism instead of the virial approach, the series expansion of thermodynamic functions with the MFD D_m as an argument can be recommended. This approach will match on a full scale the chemical equilibrium theory. Why it was not done before might be explained by difficulties of the partial densities determination from available experimental data.

2.2 Real gas from the chemical equilibrium theory point of view

As an example of the chemical reaction similar to formation of dimers from monomers, it is possible to consider the reaction of mutual transformations of NO_2 and N_2O_4 described by Linus Pauling (1970). In this reaction the equilibrium concentration of N_2O_4 is equal to the second power of the NO_2 concentration multiplied by the equilibrium constant C:

$$[N_2O_4] = C * [NO_2]^2.$$

Quite similarly, the dimer fraction density should be equal to the second power of the monomer density, D_m, multiplied by the equilibrium constant C_2 (T). More general, according to the theory of chemical equilibrium, in a real gas the molar density D_k of every cluster fraction should be proportional to the k–th power of the MFD D_m, with an equilibrium cluster formation constant $C_k(T)$.

For the first acquaintance with this variable, *Figure 1* illustrates the typical pressure dependence of the MFD in a sub-critical region.
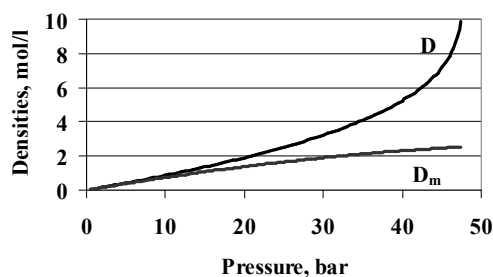

Figure 1. Comparison of the density and MFD pressure dependences for Argon at150K.

To build the bridge between virial and chemical approaches it is essential to find the way of deriving from available thermophysical data the molar density of the monomer fraction, MFD, and to base the theory of real gases on this value, as a fundamental variable.

2.3 Monomer fraction in a real gas

The monomer (monomolecular) fraction in a real gas can be defined as the part of it, consisting of the first-order clusters, in which molecules are

temporarily far enough from other molecules in such a way, that their interactions with the rest of gas might be considered negligible. The monomer fraction can be considered an ideal gas dissolved in the rest of a real gas. Its introduction into the theory of real gases is the next step after the ideal gas model. The MFD, D_m, is the number of moles of the monomer fraction in a unit of free from other particles volume. Its values may be derived from the D (P,T) experimental data with no limitations on the range of pressures.

Quite similarly, the dimer fraction in a real gas can be defined as its part consisting of pairs of particles, temporarily joined together in a relatively stable formation or repulsing from each other, with a negligibly small interaction with the rest of the gas. The dimer fraction behaves also as an ideal gas with a complex internal movement depending on a type of the intermolecular interaction mechanism. The same is valid for larger cluster fractions.

2.4 Physical and virtual clusters

It is important to note that between molecules not only attraction forces, producing real physical clusters with a positive equilibrium constant C_{pk} (T), but also repulsion forces act. In series expansions of P (D_m) or D (D_m) they produce an appearance of some virtual cluster with a negative equilibrium constant $-C_{vk}$ (T). Index p is used to mark real physical clusters and v - virtual clusters with a negative value of the equilibrium constant. So, a two-particle interaction of monomers results in the appearance of the excluded volume $C_{v2}(T)$ and attraction volume C_{p2} (T), forming the well known second virial coefficient, taken with a negative sign: $C_2(T) = C_{p2}(T) - C_{v2}(T)$. For a larger cluster its equilibrium constant C_k (T) also may be presented as a sum of physical C_{pk} (T) and virtual parts – C_{vk} (T):

$$C_k(T) = C_{pk}(T) - C_{vk}(T).$$

There is an active discussion in literature about the precise definition of the physical cluster (Harris and Ford, 2003; Kusaka and Oxtoby, 1999; Schaaf, Senger et al., 1997). But in our phenomenology the k-order cluster has pure mathematical sense, joining together its physical and virtual features in the k-order terms of series expansions D (D_m) and P (D_m). It should be noted that in supercritical fluids the virtual clusters play a more important role than the physical ones, because the attraction forces in the supercritical region are much weaker than the repulsion forces.
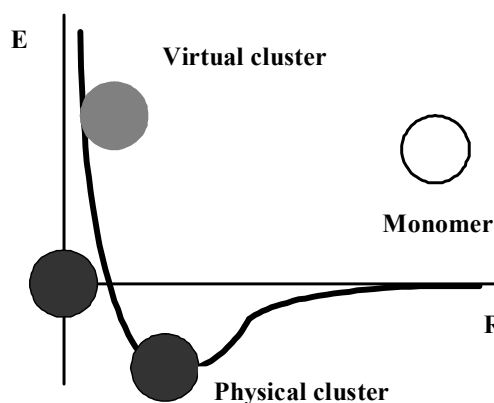

Figure 2. Illustration of different types of clusters, formed in different space-energy zones: physical cluster – in the attraction zone; virtual cluster – in the repulsion zone; monomer – free from interactions.

2.5 A principal difference between physical and virtual clusters

The *Figure 2* shows the principal difference between the two types of clusters: in a physical cluster particles spend a relatively long time in a bound state, but in a virtual cluster particles cross the attraction zone very quickly and after collision fly away. And this difference in times is measured by many orders of magnitude. That means the statistical ensemble of virtual clusters is significantly less populated than the one of physical clusters. In the quantum language the particle in a bounded state has the large density of its wave function in the vicinity of the attracting particle, but the free moving particle has its density spread all over the total volume and its density near the colliding particle is negligibly small.

Why then do the virtual clusters manifest themselves in the excluded volume that is of the same order of magnitude as the dimer formation equilibrium constant? It is because their mechanism of particles interaction is quite different from the mechanism of bonding in a physical cluster. This mechanism is of the collision type, and its consideration cannot be performed in a static picture, as in *Figure 2*.

Namely the static consideration of the repulsive interactions between two atoms leads to a false conclusion about excluded volume being equal to four own volumes of atoms. Only taking into account the dynamics of collisions is it possible to calculate the correct value for the excluded volume. And this consideration should

influence the selection of a proper MD simulation algorithm. Only the MD algorithms correctly considering the collision dynamics may give a correct value for the excluded volume.

Roughly speaking, the currently accepted static picture fixes atoms at their positions. Every fixed atom excludes from the total volume the hard sphere with a radius two times larger than its own radius and with a volume equal to eight of its own atom volumes. The division by two does not save the situation: the resulting excluded volume is still much higher than the experimental value. But in a dynamic picture, two colliding atoms rotate around their contact point with a radius equal to one atom's radius. That results in the excluded volume equal to the own atom's volume. Surely, this picture is too rough, but it shows the main difference between static and dynamic approaches.

For supercritical fluids these considerations are of greatest importance, because for them collisions of particles are much more influential than their temporary bonding. And the author's analysis of some simple supercritical fluids shows that their excluded volume is less than one own atom's volume.

3. Generalized Sackur-Tetrode Equation for the Entropy of a Real Gas

Having in mind that the monomer fraction is an ideal gas, we build the MFD determination on the equation for the entropy S_i of a monatomic ideal gas that has been suggested by Otto Sackur (1912) and Hugo Tetrode (1912), basing it on the old quantum theory. This equation in a compact form, used by Kittel (1969), is expressed as:

$$S_i = R \left(2.5 + \ln\left(V_i / V_i\right)\right) \qquad (1)$$

where V_i is the molar volume of an ideal gas, $V_q = h^3 N_A{}^4 /(2\pi MRT)^{3/2}$ - the molar quantum volume that is proportional to the third degree of the thermal de Broglie wavelength, h – Plank's constant, M – molecular weight in kg/mol, N_A – Avogadro number, R – universal gas constant.

The Sackur-Tetrode equation was a remarkable breakthrough from classical thermodynamics to the emerging quantum picture of nature and stimulated multiple theoretical and experimental investigations. It was experimentally confirmed with good precision for noble gases starting, in accordance to the third thermodynamics law, from $S = 0$ at $T = 0K$.

3.1 Gibbs energy and entropy for monatomic real gases

From Equation (1) and the thermodynamic equation for Gibbs energy of the monatomic ideal gas $G_i = 2.5RT - T S_i$ a very simple expression for G_i follows:

$$G_i = RT \ln\left(D_i V_q\right) \qquad (2)$$

For one mole of basic particles Gibbs energy equals the chemical potential. In an equilibrium state the chemical potential of basic particles does not depend on the aggregate states. So, Gibbs energy G_k for k-order fraction, including Gibbs energy G_m for monomer fraction should be the same and should coincide with Gibbs energy G for the total real gas:

$$G_k = G_m = G \, .$$

So, in a monatomic real gas

$$G = RT \ln\left(D_m V_q\right).$$

It is a key point in the calculation of the D_m values based on the experimental data $D\ (P)$.

From the equation for G the equation for entropy S of the monatomic real gas takes a form of the generalized Sackur-Tetrode equation:

$$S = H/T - RT \ln\left(D_m V_q\right) \qquad (3)$$

Here H is the molar enthalpy of a real monatomic gas.

Equation (3) has been derived on a pure thermodynamical basis and does not require any assumptions about interatomic forces. It is seen that the logarithmic part of the equation contains information only about the monomer fraction; all contributions of other cluster fractions enter the total enthalpy of the gas. It may sound surprising, but this equation provides an excellent correlation with experimental data also for supercritical fluids and liquids. It confirms the correctness of the D_m computation in all available range of pressures.

Figure 3 illustrates high precision of the entropy calculation with the generalized Sackur-Tetrode model at subcritical and supercritical pressures for monatomic substances. It is clear that deviations between theoretical and experimental values, being four orders of magnitude less than the total entropy change with pressure, originate from experimental, rather than from theoretical errors.
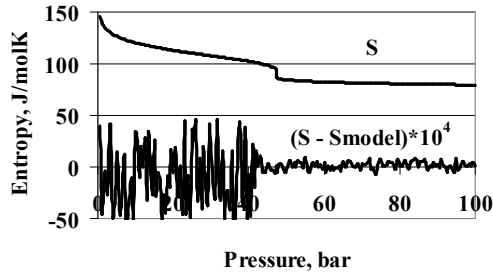
Figure 3. Entropy values and multiplied by factor 10^4 their deviations from the predicted by the generalized Sackur-Tetrode equation values for argon at 150K.

3.2 Gibbs energy for molecular gas

It is useful to divide Gibbs energy on its translational, G_{tr}, and internal movements, G_{int}, parts. The second part can be prescribed for any pressure as a limit of $G - G_i$ at pressures coming to zero. It does not mean that the internal movements' contributions in G do not depend on P, but all changes of these contributions with pressure are included in changes of the translational part.

To be correct, the internal movements' part, G_{int}, includes also reference values: E_0 for energy and S_0 for entropy, depending on the selected system of measurement. In our approach the energy measurement starts from zero energy for a freely moving particle, and entropy starts from zero value for the ground state of the substance under investigation at $T = 0K$.

The translational part of G can be found as:

$$G_{tr} = G - G_{int}.$$

The translational part of G_m, $G_{mtr} = 2.5RT - T S_{mtr}$, for the monomer fraction, as an ideal gas, can be written:

$$G_{mtr} = RT \ln(D_m V_q).$$

Therefore, the translational part of G for total gas corresponds to the equation:

$$G_{tr} = H - E_{int} - T(S - S_{int}) = RT \ln(D_m V_q). \quad (4)$$

Here H is the molar enthalpy, E_{int} and S_{int} – the molar energy and entropy of the molecular internal movements in the real gas, plus E_0, S_0, depending on the system of measurement.

This equation leads to the generalized Sackur-Tetrode equation for entropy of a molecular real gas:

$$S = (H - E_{int})/T + S_{int} - RT \ln(D_m V_q). \quad (5)$$

Figure 4 illustrates high precision of the entropy calculation with the generalized Sackur-

Tetrode equation at subcritical and supercritical pressures for molecular substances.
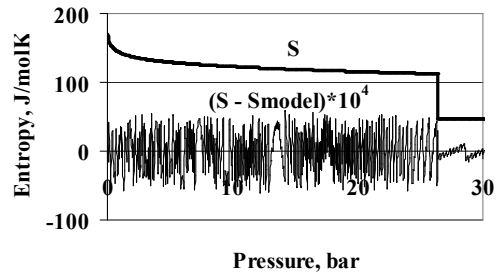

Figure 4. Entropy values and multiplied by factor 10^4 their deviations from the predicted by the generalized Sackur-Tetrode model values for water at 500K.

Equation (5) appeared after the author's multiple attempts to find an appropriate approximation for $S (P,T)$ (Sedunov, 2001). But in a final version it is free from any approximations and assumptions about the intermolecular interaction mechanisms. All pressure dependent details of these mechanisms are hidden in the enthalpy of a real gas.

High precision of the MFD based entropy calculation from enthalpy, density, pressure and temperature data permits also the computing of Gibbs and Helmholz energies from these initial values with a high precision and with no limitations on the pressure range.

3.3 Master equation for MFD computation

Keeping in mind that G_{int} is independent of pressure, it is possible to apply the thermodynamic equation

$$\partial G / \partial P|_T = V$$

only to G_{tr}, given by Equation (4), and to write a differential equation for the MFD:

$$\partial D_m / \partial P|_T = D_m / DRT. \quad (6)$$

Equation (6) can be named the master equation for MFD computation utilizing a set of data $D_j (P_j, T)$ from any available database.

The numerical integration of this equation for an isothermal set of data $D_j (P_j, T)$ returns the $D_{mj} (P_j, T)$ values for the selected temperature and for all pressure values This integration is a very delicate procedure and requires a high precision of the initial data $D_j (P_j, T)$ with a small enough value of the pressure step $P_{j+1} - P_j$.

It is impossible to use a simple initial condition $D_m = D = 0$ at $P = 0$, because it results in division by zero. As the initial condition for integration of the master Equation (6), we suggest the equation $D_m = 2P/RT - D$ that can be valid

only in the region of small values of P, where $ABS\ (P/RT - D)$ is much smaller than D.

As a source of experimental data, the permanently updated online database of the US National Institute of Standards and Technology (NIST, 2007) for monatomic and molecular gases was used. This database contains comprehensive data for 75 substances in gaseous and fluid states given with 5 decimal digits.

Negligible value of deviations between theoretical and experimental data for entropy, illustrated by *Figures 3* and *4*, was proven on several substances with hundreds of temperature points and thousands of pressure values. It provides a reliable confirmation that the computational method and procedures are quite correct. Their precision will grow together with growth of the initial databases precision.

High precision both of the MFD and MFD-based thermodynamic functions computation opens ways for the MFD incorporation in the databases for monocomponent substances. This incorporation may serve as an independent method of the calorimetric data verification and correction.

3.4 MFD at high pressures

In a supercritical fluid, where the molar volume approaches a constant value V_0, the MFD grows exponentially with pressure as the reflection of the Gibbs energy approximately linear growth in this region:

$$G = G_0 + V_0 P .$$

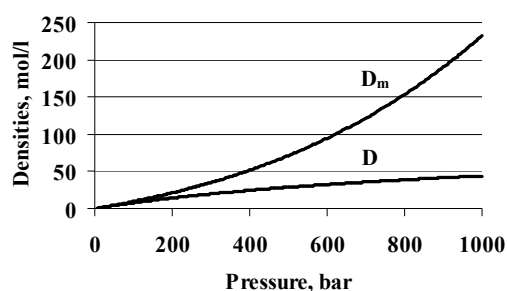*Figure 5* illustrates the exponential growth of the MFD at high pressures.

Figure 5. Exponential growth of the MFD, D_m, and saturated growth of the density, D, at high pressures in the supercritical helium at 140 K.

In the region of high pressures the precision of the theoretical prediction for entropy values is still very high, as shown in *Figure 6*.
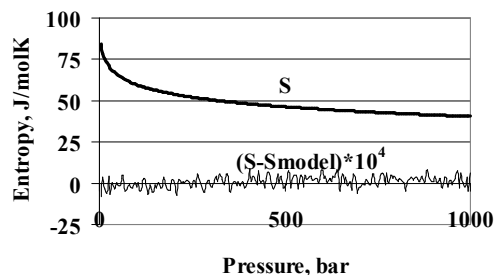

Figure 6. Entropy values and multiplied by factor 10^4 their deviations from the predicted by the generalized Sackur-Tetrode equation values for supercritical helium at 140 K.

It confirms an applicability of the MFD and MFD-based computations in the whole investigated range of pressures. There is no obvious and simple interpretation of the MFD nature at high pressures. But this difficulty should not become an obstacle before the practical utilization of the MFD. A detailed investigation of supercritical fluids shows that at high pressures the reverse to the MFD value, the particular molar volume, that may be named 'gettable', has clearer physical sense than MFD. But this question requires special investigation in a separate paper.

4. Utilization of MFD as an Argument for the Density and Pressure Series Expansions

Master Equation (6) provides a theoretical basis for determination of the equilibrium constants C_k from the coupled series expansion for $P(D_m)$ and $D(D_m)$.

With a found set of data $D_{mj}\ (P_j , T)$ for a fixed T the total pressure P can be expressed as a series expansion:

$$P = RTD_m\left(1 + \sum_{k=2}^{\infty} C_k D_m^{(k-1)}\right) \qquad (7)$$

that may be interpreted as a sum of partial pressures of fractions. As has already been noted, this equation contains both physical and virtual parts of the C_k.

From the master Equation.(6) the total density D can be expressed in a similar way:

$$D = D_m\left(1 + \sum_{k=2}^{\infty} C_k D_m^{(k-1)}\right) \qquad (8)$$

Here the series expansion coefficients contain the factor k in accordance with Equation (6).

So, for D (D_m) and $P(D_m)$ a system of coherent and cross-correlated Equations. (7, 8) is valid. This coherence and cross-correlation help to find the equilibrium constants C_k (T). They provide the possibility of suppressing polynomial oscillations inherent to ordinary virial expansions.

4.1 Experimental data processing

At the first step, the range of P_j (T), where only the terms of the second and third orders are essential, is selected to find C_2 and C_3. Then, the working range of P_j (T) is step-by-step expanded to find C_4 and C_5 and to proceed further (Sedunov, 2007c).

Then the found values of C_k (T) are used to compare the polynomial approximations for pressure and density with their real values. The computation process may be regarded as correct, if the deviation of the approximation from experimental data is of the same order of magnitude as the occasional spread of the initial $D_j(P_j, T)$ data.

For the moment, the next real gases have been investigated: helium, parahydrogen, argon, nitrogen, methane, water and alkali-metal vapors. As an example of a typical picture, *Figure 7* shows temperature dependences of equilibrium constants for parahydrogen, demonstrating the asbsence of the fourth term in the joint series expansion.
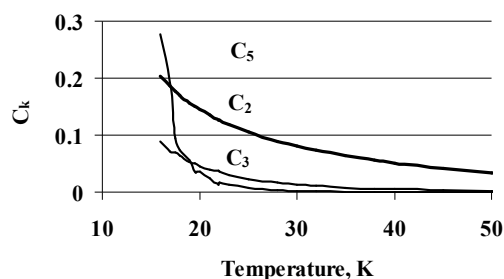

Figure 7. Temperature dependence of equilibrium constants C_k for parahydrogen with missing C_4 constant.

4.2 Missing terms in the joint series expansion

For all investigated gases a discrete structure of the series expansion is discovered. That means an absence of some terms in the power expansions. So, for argon, parahydrogen, methane and nitrogen it was impossible to notice any traces of the C_4 (T), but in water this coefficient has a noticeable value that reflects a quite different type (polar instead of the van der Waals') of the intermolecular interaction. The very possibility of throwing away the numbers $k,$ not presented in the joint series expansion, prevents the series expansion computer program catching the nonexistent numbers.

It should be noted that the discrete structure of the MFD-based series expansions disappears in ordinary virial expansions. That means the virial expansions provide less information for the cluster formation mechanism.

The physical interpretation of the missing terms phenomenon is not possible at this level of knowledge. A wider database of C_k (T) for many real gases is needed to be collected, significantly differing one from another, just to create a solid basis for future generalization. But it is clear already now that a simple model of particles interaction via their attraction-repulsion potential depending on the distance between their centers cannot explain missing of some terms. Quite another model of particles interaction is needed to describe this phenomenon.

4.3 Polynomial oscillation suppression

Unlike virial expansion, the cross-correlation of two coherent equations prevents falling into the well known problem of polynomial oscillation at series expansions. The series expansion itself may be related to a class of incorrect mathematical problems. That means a large instability of final results at small deviations of initial data. In series expansions this instability takes the form of oscillating polynomials, like Chebyshev's polynomials with small amplitude in some range of arguments but with large series expansion coefficients. These error coefficients grow very fast with growth of the number k and limit possibilities of the virial expansions by the first two virial coefficients. For higher order virial coefficients, as a rule, the errors are comparable with their values.

In our case, we find equilibrium constants C_k from a pair of Equations. (7, 8). The possible error polynomials are different for every equation, and it helps to suppress them. That results in a higher precision of the high order coefficients. In some cases it is possible to reach numbers as large as 10.

4.4 Applicability of the equilibrium constants for the nucleation problem

The presentation of the real gas pressure and density as the sums of partial quantities was used by Ford (1997) to estimate the clusters' populations in the supersaturated region.

When coefficients C_k (T) are found, it becomes possible to step from the investigated range of P in a supersaturated state of a real gas just to estimate the clusters population distribution in this region. It may be used for the nucleation processes research (Ford, 2004), particularly for modification of Ford's (1997) method of virial coefficients utilization to estimate initial clusters population.

5. Conclusion

The introduction of the monomer fraction density (MFD) expands the power of the computer assisted analysis of a wide series of thermodynamic functions of real gases that permits throwing more light on the interactions of atoms and molecules.

Approximations for Gibbs energy and entropy, based on the found values for D_m and C_k, possess smaller spreads than the database values resulting from calorimetric measurements. It opens the way to correct the existing databases.

The MFD sets of data can be added to existing databases to expand their cognitive power and practical value.

The found facts inspire and provide directions for more profound experimental and theoretical studies of real gases and condensed matter.

Possible practical applications of this research may be in the next fields:

- more effective utilization of databases on thermophysical properties of real gases in computer aided design and control of chemical and material technologies;

- an improved precision of thermo-physical databases through the cross-correlation of different thermodynamic functions and MFD;

- stimulation and targeting of new experimental research in order to make precise the details of the interatomic interaction mechanisms and van der Waals forces;

- new approaches to teaching thermo-dynamics of real gases.

Nomenclature

MFD   Monomer fraction density
MD   Molecular dynamics
D Molar density of a real gas, *mol/l*
P Pressure, *bar*
k Number of particles in the cluster and the order of the series expansion term
D_k Partial molar density of the k-order cluster fraction, *mol/l*
D_m Monomer fraction density, *mol/l*
P_k Partial pressure of the k-order cluster fraction, *bar*
$C_k(T)$ Equilibrium k-order cluster formation constant, reflecting both attraction and repulsion forces
E Internal energy, *J/mol*
G Gibbs free energy, *J/mol*
S Entropy, *J/(mol K)*
H Enthalpy, *J/mol*
G_{tr} Translational part of the Gibbs free energy
G_{int} Intramolecular part of the Gibbs free energy
E_0 Zero energy level for a freely moving particle as a reference value for the selected system of measurement
S_0 Zero entropy level for the ground state of the system as a reference value for the selected system of measurement
V_i Volume for a mole of an ideal gas, *l/mol*
V_q Molar quantum volume for the mono-molecular fraction, *l/mol*
h Plank's constant
M Molecular weight, *kg/mol*
N_A Avogadro's number, *1/mol*
R Universal gas constant, *J/(mol K)*.

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