
The Linear Chain Clusters in Real Gases

Boris Sedunov^{1*}

DOI: 10.9734/bpi/ nicst/v12/8200D

ABSTRACT

The chapter describes the new class of linear chain clusters, discovered by the author, and the methods of their properties evaluation. In real gases exist different types of clusters: linear with a minimal number of bonds between particles and tightly bound two and three dimensional clusters. The experimental data analysis for many pure gases shows wide zones of temperature and density, where the linear chain clusters dominate. The potential energy density series expansion by the monomer fraction density at moderate densities of real gases returns cluster bond parameters and their equilibrium constants, which may be attributed to this new class of clusters. The monomer fraction density based computer aided analysis of precise thermophysical data for pure fluids discovers wonderful properties of these unknown cluster structures in real gases. An extrapolation of these loosely bound clusters' properties to larger densities provides a selection of densely bound three dimensional clusters in sub- and supercritical fluids in general and especially in the CO₂. It is important to know the clusters structure and parameters in this gas, widely used in supercritical fluid technologies. Step-by-step movement from diluted to dense gases discovers properties of large three dimensional clusters with numbers n of particles up to the level of one thousand. The logarithmic method to estimate the averaged numbers n of particles in three dimensional clusters is developed to study the mechanism of the soft structural transition between dominating cluster fractions with neighbor numbers n and between the gas-like and liquid-like supercritical fluids.

Keywords: Real gas; supercritical fluid; bond energy; equilibrium constant; carbon dioxide.

*To understand the actual World as it is,
not as we should wish it to be,
is the beginning of wisdom.*

Bertrand Russell

1. INTRODUCTION

In this chapter we develop the phenomenological approach to investigations of the new cluster structure in neat real gases. The used here computer aided analysis of precise experimental thermophysical data for pure fluids is based on the monomer fraction density [1] as the main variable for series expansions of equilibrium thermophysical values. Only this variable may be used as an argument for series expansions of thermophysical values in their application to cluster fractions in pure fluids [2], because only this type of series expansions corresponds to the Mass action law [3]. At this moment the computer simulation of the clusters' properties based on model potentials has no solid experimental basis, such as the atomic and molecular interaction parameters.

The physics of clusters in real gases benefits from the computational analysis of precise data, contained in the NIST Webbook for Thermophysical Properties of Fluids [4]. By this way an unknown type of chain clusters, found in many equilibrium pure gases, such as noble and polar gases, CO₂, N₂, F₂ and Alkanes has been discovered [5]. These clusters are 1D polymer-like linear chains of n molecules possessing $(n - 1)$ pair bonds between them. They dominate over 3D clusters at densities

¹Computer and Information Systems Department, Russian New University, Moscow, Russia.

*Corresponding author: E-mail: Sedunov.b@gmail.com;

reaching the fifth of the critical density and at temperatures over the middle point between the triple and critical points. The domination of chain clusters in such a wide zone of densities and temperatures is a generous present of Nature opening possibilities to investigate the clusters' formation physics. In this zone the parametric Equation of State (EoS) was formulated basing on the discovered law for chain clusters formation.

The extraction of the molecular interaction and clusters parameters from experimental data [6,7] is the inverse mathematical problem [8] suffering from errors in initial data and in algorithms of the data processing. Therefore, the used for the cluster properties extraction experimental data should be very precise. We have selected for our analysis the thermophysical data from the NIST Webbook [4], which are very precise and mutually correlated. In this research special measures have been taken to diminish the influence of the initial and digital processing errors on the final results.

The clusters now attract a large attention of researchers. Linn Yarris from Berkeley Lab even named clusters as a new state of matter [9]. Taking into account that attempts to understand the clusters nature last more than a century, we may say that the clusters are still unknown state of matter [10]. They are intermediate structures between free moving particles in ideal gases and bound particles in condensed matter. Moving step-by-step from diluted to more and more dense gases we understand the thermodynamics of gases with more and more complex structures of clusters [11].

The widely used in science and practice virial equations are useful tools mainly to generalize and systemize the experimental data. But they do not provide a clear physical interpretation of virial coefficients. Their arguments, pressure P or density D , are the mixtures of partial quantities P_n , D_n related to n -particle cluster fractions. Therefore, the virial form of series expansions does not apply the Mass action law to clusters and returns the expansion term as a combination of different cluster fractions contributions. So, the conclusions from virial expansions about the nature and parameters of clusters are misleading. Richard Feynman wrote [12] that the virial expansions based clusters investigation program had been stopped.

The developed by the author [13,14] thermal analysis of regularized experimental thermophysical data method provides a physically clear vision of the cluster fractions' structure in pure real gases. The method is based on the series expansion of equilibrium thermophysical functions by the monomer fraction density D_m , introduced by the author in the family of thermophysical properties of fluids [1, 2]. The method is related to the so called inverse mathematical problem [8] arising in the processes of hidden parameters extraction from experimental data and for this reason is very sensitive to errors in experimental data. But utilization of regularized data from the NIST Webbook [4] permits to solve the problem successfully.

The most informative thermophysical function for the clusters' properties analysis happened to be the potential energy $U = (E(T, P) - E(T, 0))$ [6], where $E(T, P)$ and $E(T, 0)$ are internal energies of real and ideal states of a gas at a temperature T . Its positive density $(-UD)$ divided by the second power of the monomer fraction density D_m , $W_{2+} = (-UD) / D_m^2$, is the function $W_{2+}(D_m)$ to energy density series expansion.

1.1 Useful Definitions

Basic particles - the particles of the fluid that reflect the chemical nature of the fluid independently on their inclusions in different cluster fractions;

Free moving particles - the monomers and clusters conserving their kinetic energy and moment while moving in a gas without collisions;

Monomers - the basic particles, temporarily non interacting with other free moving particles;

Clusters - the agglomerations of basic particles, bound by atomic or molecular attractive interactions and conserving their number of particles while moving in a gas without collisions;

Cluster isomer - the n-particle cluster with a definite number of bonds between particles;

Linear chain cluster - the cluster isomer, which particles possess no more than two bonds inside the cluster;

Tightly bound cluster - the cluster isomer, some particles of which possess more than two bonds inside the cluster;

Gas potential energy - the difference between the gas molar internal energies at a given pressure and zero pressure;

Potential energy density - the gas potential energy by the gas molar density product;

Cluster bond energy - the average energy needed to totally dissociate cluster on monomers;

Pair bond energy - the average bond energy between two particles;

Soft structural transition - the transition between two cluster isomers with different bond energies in a wide range of temperatures or the transition between dominating clusters with different particles numbers and gas-like and liquid-like supercritical fluid structures at a supercritical temperature in a wide range of pressures.

Normal gas - the gas with a spherical symmetry of atomic or molecular interactions;

Anomalous gas - the gas with directional bonding between particles.

1.2 Small Linear Clusters in Normal Gases

The first authors' attempts to extract the clusters' bond parameters brought reliable results only for small clusters with numbers of particles from two to four. For growing numbers of particles in clusters the results were less stable and reliable.

In normal gases with a spherical symmetry of interatomic bonds, such as Helium, linear clusters dominate among small clusters. It is seen from the Fig. 1, which shows the logarithms of the potential energy density series expansion terms W_n [6] in their dependence on the reverse temperature $1000/T$ for small clusters. The tangents of diagrams' slopes give the average cluster bond energies, E_n in K.

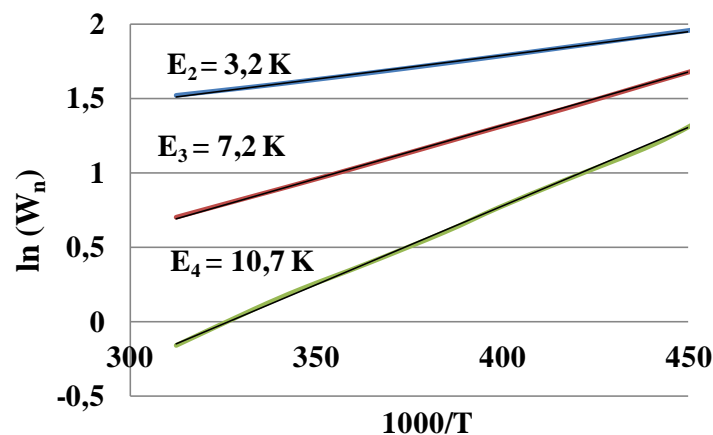


Fig. 1. The logarithms of the potential energy density series expansion terms W_n in their dependence on the reverse temperature $1000/T$ for dimers, trimers and tetramers in Helium in the temperature range 2,2 - 3,2 K

The clusters' bond energies grow with the number n atoms in a cluster almost linearly, Fig. 2. The dependence $E_n(n)$ is close to:

$$E_n(n) = E_2(n - 1) \tag{1}$$

There is a temptation to extend the straight line at the Fig. 2 to larger numbers n . While developing the method to analyze large tightly bound clusters the author has discovered a wonderful class of linear chain clusters [5], which properties may be extrapolated to the near critical density, thus permitting to separate the tightly bound clusters from the loose clusters influence [5,15]. The straight line at the Fig. 2 is supposed to be extended for $n > 4$ and the Equation (1) seems to be valid for linear clusters with any number of atoms. This chapter aims to build the method of clusters' properties analysis at moderate densities of gases and to use this knowledge to select and analyze the contribution of large three dimensional clusters in thermophysical properties of supercritical fluids.

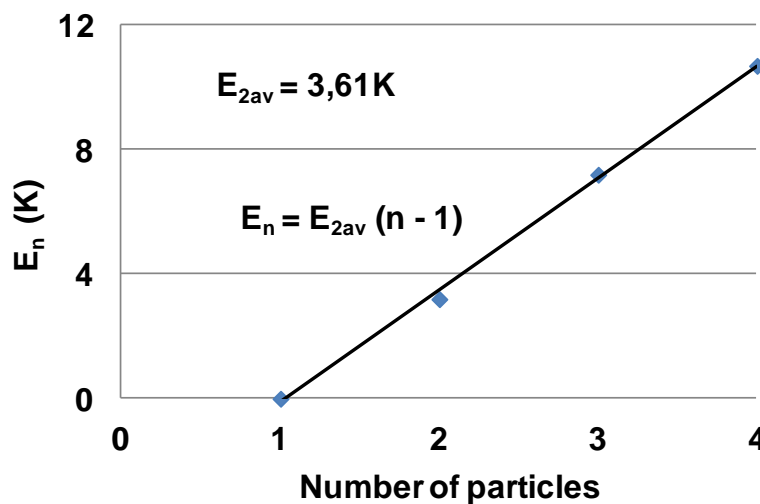


Fig. 2. The dependence of clusters' bond energies on the number of atoms in clusters $E_n(n)$ in Helium for temperature range 2,2 - 3,2 K : estimated from experimental data E_n - markers, trend - straight line

2. THE PROPERTIES OF CHAIN CLUSTERS

It was a great challenge for the author to find properties of large clusters that play an important role in technological gases and in supercritical fluids [16]. Here we demonstrate the unknown type of chain clusters, discovered in all equilibrium pure gases, presented in the NIST Webbook [4].

These clusters are 1D polymer-like linear chains of n molecules possessing $(n - 1)$ pair bonds between them [5,17]. They dominate over 2D and 3D clusters at densities up to one fifth of the critical density and at temperatures over the middle point between the triple and critical points. This middle point approximately limits the zone of existence for clusters with unusual giant bonds, such as tetramers in the low temperature Water vapor [13] or trimers in Ne [18]. For gases without giant bonds in clusters the temperature range of the chain clusters domination zone takes all range, presented in the Webbook, starting from the triple point.

The domination of chain clusters in such a wide zone of densities and temperatures is a valuable feature opening possibilities to investigate the clusters' formation physics. For this zone the Equation of State (EoS) was formulated basing on the discovered law of chain clusters formation. To extract properties of chain clusters from precise experimental data a special mathematical method was developed and the zones of temperatures and densities, where they dominate over 3D clusters, have been determined [17].

2.1 The Discovery of Chain Clusters in Real Gases

The first authors' attempts to extract the clusters' bond parameters brought reliable results only for small clusters with numbers of particles from two to four. For growing numbers of particles in clusters the results were less reliable. It was a great challenge for the author to find properties of large clusters, which play an important role in technological gases and in supercritical fluids. All attempts to expand in a series by D_m a highly nonlinear W_{2+} / W_2 function for Carbon Dioxide, shown at the Fig. 3, brought unstable results.

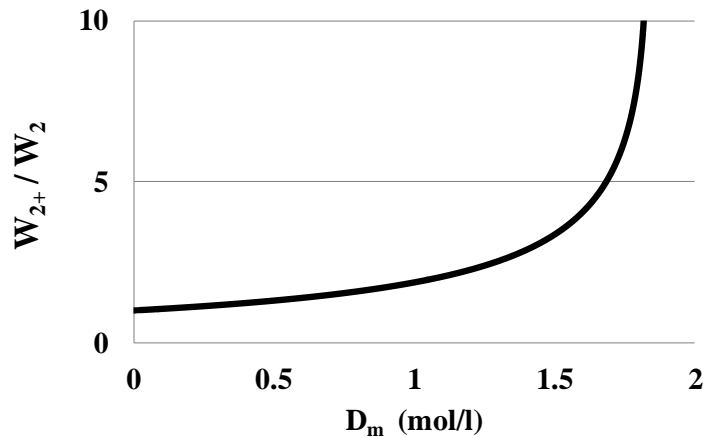


Fig. 3. The W_{2+} to W_2 ratio dependence on D_m in CO_2 at $T = 300$ K and pressures up to 67 bar demonstrating a challenging complexity of the series expansion at extra high nonlinearity

Suddenly, for Carbon Dioxide an inversion of the no dimensional function W_{2+} / W_2 made a breakthrough [5] to larger clusters. The author noticed that the inversely proportional function W_2 / W_{2+} , shown at the Fig. 4, keeps a wonderful linearity in a wide range of D_m , up to 1.4 mol/l. At $T = 300$ K in CO_2 the upper boundary of this range corresponds to large values for pressure, $P = 38$ bar, and gas density, $D = 2$ mol/l. So, the inverse potential energy density function became the key to solve the inverse problem of cluster properties extraction from precise experimental thermophysical data.

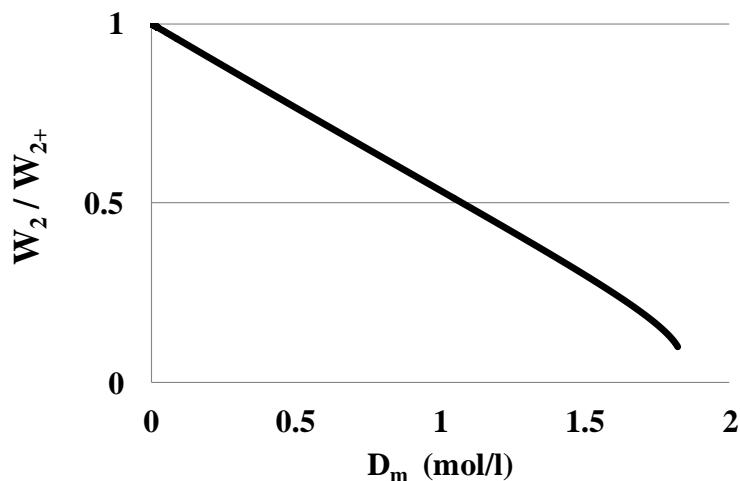


Fig. 4. The W_2 to W_{2+} ratio linear dependence on D_m in CO_2 at $T = 300$ K demonstrating the correspondence of equilibrium coefficients W_n to the geometric progression law for pressures up to 38 bar

The analysis shows the independence of the responsible for the chain growth characteristic volume V_u on the chain length. The product of this volume by the Monomer Fraction Density [1] has proven to be a common ratio of the geometric progression law for a row of chain clusters with growing numbers of particles at a fixed T. The geometric progression law permits to extrapolate the chain clusters' contribution in the total potential energy up to near critical density. By this way we can separate the 3D clusters' contribution in potential energy from the 1D clusters' contribution. It opens possibility to investigate the equilibrium 3D clusters at high densities of gases.


2.2 The Geometric Progression Law for Chain Clusters

A linear part of the graph at the Fig. 4, with V_u being the tangent of slope of the line, results from the geometric progression law for terms of the W_{2+}/W_2 series expansion with a no dimensional common ratio $V_u D_m$. The linearity tells that $W_{2+}/W_2 = (1 - V_u D_m)^{-1}$ and the n-order coefficients W_n of the series expansion obey to the geometric progression law. This linearity opens the way to investigation of equilibrium n-particle clusters at large pressures and densities of a real gas. In the zone of the W_2 / W_{2+} -linearity there is no need to expand the W_{2+} in series. The coefficients W_n may be found directly from the geometric progression.

An indication on the geometric progression, the linearity of the W_2 to W_{2+} ratio dependence on D_m , had been noticed for all investigated by the author pure gases, presented in the NIST Webbook [4]. This law tells that an attachment of the next monomer to the n-particle cluster has a universal mechanism for all numbers n with the same bond energy E_2 for all bonds in a chain [19].

The only explanation of this remarkable fact is the 1D chain type of clusters, Table 3. An absence of branches on the chain is not understandable from the current point of view on the Molecular Interactions in real gases. It tells about a new mechanism of the particle attachment to ends of an existing chain.

Table 3. The 1D polymer-like chain clusters and the geometric progression law for their equilibrium coefficients [5,17,19]

The chain clusters				
Number of particles in a cluster	2	3	4	n
Number of bonds	1	2	3	n - 1
Equilibrium coefficients for potential energy density	W_2	$W_2 V_u$	$W_2 V_u^2$	$W_2 V_u^{(n-2)}$
Bond energy	E_2	$2E_2$	$3E_2$	$(n-1)E_2$

In Propane the linearity of W_2 to W_{2+} ratio dependence on D_m was shown for a T range between 280 and 500 K and P up to 5.8 bars, Fig. 5.

In the isothermal data analysis we can select larger maximal values for pressure for different temperatures. The analysis at high pressures gives the boundary of the 1D clusters zone, beyond which the contribution of 3D clusters becomes noticeable and the domination of 1D chain clusters terminates. In enlarged range of pressure in Propane at T = 360 K the deviation from the W_2 / W_{2+}

versus D_m linear dependence, seen at Fig. 6, starts at $D_m = 0.6$ mol/l. It corresponds to the total density D near 1 mol/l.

The shown at the Fig. 6 bend of graph at the gas density over 0,6 mol/l demonstrates the soft structural transition from linear to 3D clusters [20].

In Water vapors the presented at the Fig. 7 dependences taken at 460, 600 and 1200 K demonstrate a wonderful linearity in wide ranges of pressures and densities. The maximal density of the linearity range for the W_2 / W_{2+} dependence on D_m also reaches approximately one fifth of the critical density.

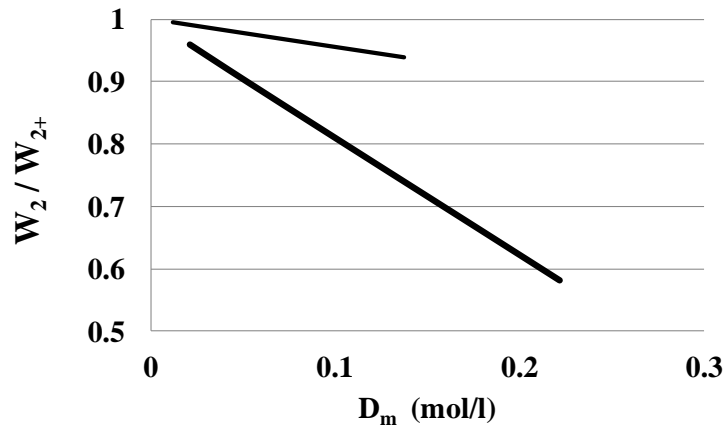


Fig. 5. The linear W_2 to W_{2+} ratio dependence on D_m demonstrating correspondence of the chain clusters in Propane to the geometric progression law at P from 0 to 5.8 bar; $T = 280$ K (thick line) and 500 K (thin line)

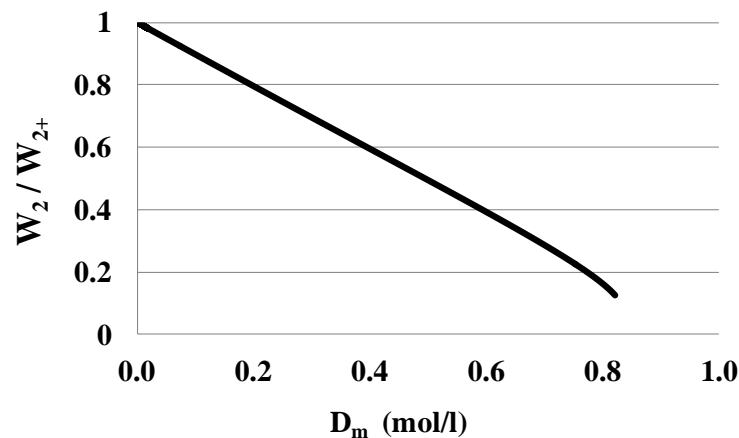


Fig. 6. The W_2 to W_{2+} ratio dependence on D_m in Propane at $T = 360$ K in enlarged pressure range up to 35.5 bar, demonstrating high linearity up to $D_m = 0.6$ mol/l

The maximal pressure for $T = 600$ K is equal to 120 bar, for 1200 K it is 400 bar. For $T = 460$ K the maximal pressure is limited by its saturation value. The three lines clearly show the temperature dependence of their tangents of slope. That means that the chain growth characteristic volume V_u strongly depends on temperature.

The V_u temperature dependence is clearly seen for Noble gases, Fig. 8. In Noble gases the zone of 1D chain clusters domination is also wide. The analysis of Isochoric data for Krypton at densities up to 0.6 mol/l shows that the W_2 / W_{2+} dependence on D_m is linear in a wide zone of temperatures: 153 –

750 K. So, clusters in many dense gases show universal behavior in the zone, where W_2 to W_{2+} ratio linearly depends on the monomer fraction density, D_m .

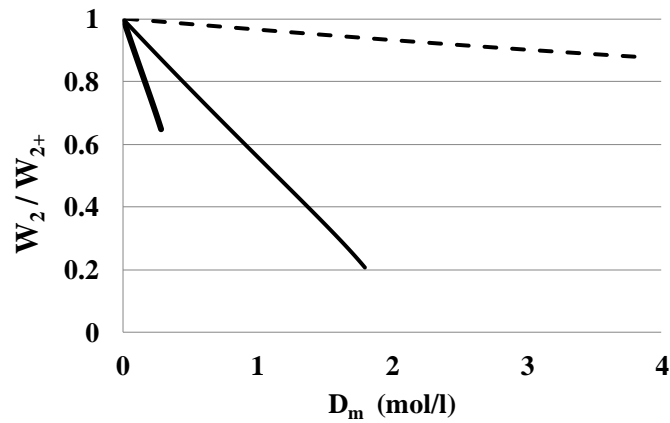


Fig. 7. The W_2 to W_{2+} ratio dependences on D_m in Water at $T = 460$ (thick line), 600 (thin line) and 1200 K (dashed line)

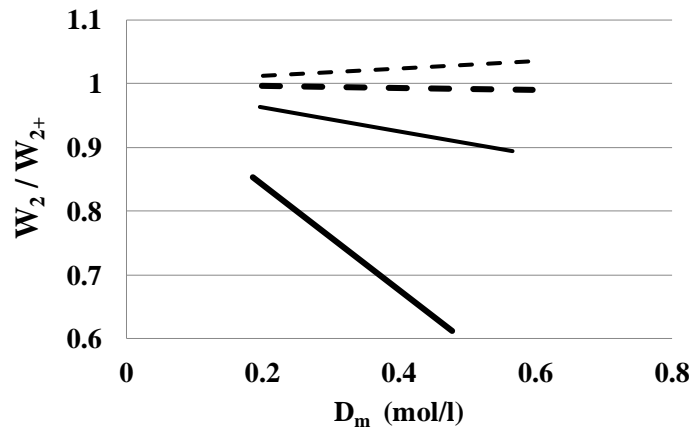


Fig. 8. The W_2 to W_{2+} ratio dependences on D_m in Krypton at $T = 153$ (thick line), 300 (thin line), 501 (thick dashed line) and 750 K (thin dashed line).

It is the class of chain clusters possessing a universal law of a new particle attachment to the ends of a chain. And this universality confirms an importance of the D_m utilization as an argument for series expansion of thermophysical values.

We will name the linear part of the W_{2+} function as the W_{2+} .

The linear parts of graphs for W_2 / W_{2+} at Figs. 4-8 correspond to the law:

$$W_2 / W_{2+} = 1 - V_u(T) D_m. \quad (2)$$

The inversely proportional to the W_2 / W_{2+} function, W_{2+} / W_2 function, corresponds to the equation (3):

$$W_{2+} / W_2 = (1 - V_u D_m)^{-1}. \quad (3)$$

A simple form of the expression (3) opens a wonderful possibility to investigate the new class of clusters with this remarkable behavior, occupying a very wide temperature-density zone. The equation

(3) is a sum of geometric progression with a common ratio $V_u D_m$ and infinite number of terms; $V_u(T)$ is close to four apparent equilibrium constants $C_2(T)$ [13] for PDT properties: $V_u(T) \approx 4 C_2(T)$.

The common ratio in the chain clusters domination zone is smaller than 1. Therefore, the contribution of clusters in the total potential energy quickly falls with their length. Practically the row of chain clusters may be cut at some number without noticeable errors in estimation of the total potential energy. But it demonstrates an absence of limitations on the chain length. The extra long chains at a change of temperature may serve as the seeds or nuclei of condensation.

2.3 The Geometric Progression Law for Pressure-Density Coefficients

For larger numbers of particles in clusters the difference between experimentally based $C_n(T)$ and model values becomes much greater. $C_n(T)$ are the n -order series expansion coefficients, found from the system [10,12,13] of series expansions of pressure and density by D_m and reflecting n -particle interactions:

$$P = RT \sum C_n D_m^n, \tag{4}$$

$$D = \sum n C_n D_m^n, \tag{5}$$

$$\partial D_m / \partial P|_T = D_m / (RTD). \tag{6}$$

The system of equations (4-6), with $C_1 = 1$ may be interpreted as an expression of pressure and density through the sums of partial terms, reflecting n -particle interactions. Unlike widely used virial expansions, the system (4-6) is physically correct and corresponds to the Mass Action Law.

The Equations (4-6) give us the series expansion for the total number of bonds per unit volume in all chain cluster fractions:

$$D - P/RT = \sum (n-1) C_n D_m^n. \tag{7}$$

In chain clusters the total number of bonds is proportional to the potential energy density, for which we have the geometric progression law. So, the series expansion coefficients for the $D - P/RT$ function should also correspond to the geometric progression law. As an analog of the W_{2+} function, we will study the C_{2+} function; $C_{2+} = (D - P/RT) / D_m^2$. Its zero density limit is the pair interaction coefficient $C_2(T)$. We will study the linearity of the C_2 to C_{2+} ratio at a fixed temperature. For all investigated gases the linear dependence of the C_2/C_{2+} on D_m in the chain clusters domination zone exists. The Fig. 9 shows the C_2/C_{2+} dependence on D_m for Xenon at $T = 160$ K.

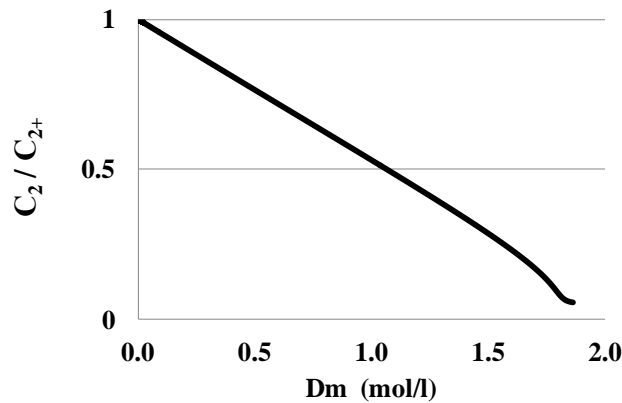


Fig. 9. The C_2 to C_{2+} ratio dependence on D_m in Xenon at $T = 300$ K

The deviation from the linearity at large densities results from a growing influence of the 3D clusters. The characteristic volume $V_p(T)$, found from the tangents of slope slightly differs from the $V_u(T)$ and $4C_2(T)$. It is seen from the Fig. 10 for Xe.

The nature of the differences between the three graphs needs to be investigated.

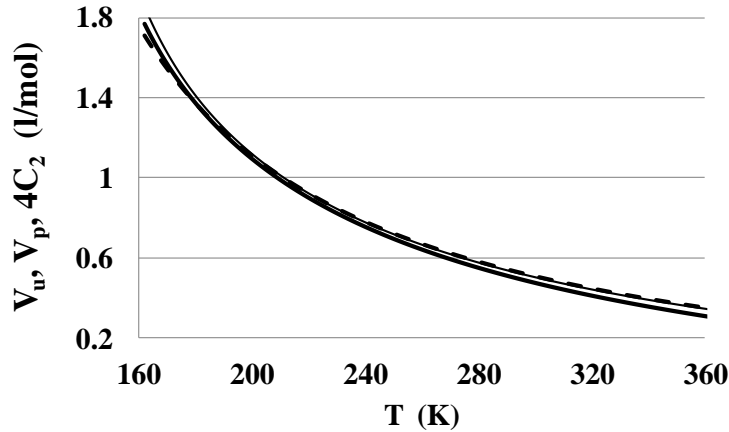


Fig. 10. The $V_p(T)$ (thick line), $V_u(T)$ (thin line), and $4C_2(T)$ (dashed line), in Xenon

2.4 The Zone of Chain Clusters Domination

The discovered for all investigated dense gases linearity of the W_{2+}^{-1} function of D_m tells about an existence of an infinite row of 1D, polymer like, chain clusters in the zone of their domination [19]. At the Fig. 10 the zone of 1D chain clusters domination in the Water vapor is depicted. At low temperatures the zone is limited by $T_m = (T_{tr} + T_{cr}) / 2$ that is the middle point between the triple and critical points. At this temperature the contribution of clusters with giant bond energies becomes negligible. But in gases without giant bonds the zone starts from the triple point.

The analysis of experimental data for all gases with giant bond clusters shows that the chain clusters dominate over 3D clusters at temperatures T above the middle point T_m between the triple T_{tr} and critical T_{cr} points,

$$T_m = (T_{tr} + T_{cr}) / 2, \quad (8)$$

in a wide range of densities D , up to one fifth of the critical density D_{cr} , Fig. 10. At $T < T_m$ the saturation density is so small that the presence of linear clusters with $n > 4$ cannot be noticed. So, at these temperatures it is useless to discuss the long row of chain clusters.

2.5 The EoS for the Chain Clusters Domination Zone

In science and education the ideal gas EoS is widely used. It is understandable from both physical and statistical points of view. But its predictions do not correspond to the precision of experimental data for real gases, starting from very low densities. The next shortcoming of the Ideal EoS is the ignoring of intermolecular forces. For practical needs there are multiple empirical EoS for real gases, but many of them, being precise, do not reflect the physics of molecular interactions in gases.

The equation for the number of bonds per unit volume in the chain cluster zone is the sum of geometric progression:

$$D - P/RT = C_2 D_m^2 / (1 - V_p D_m). \quad (9)$$

Therefore, the coefficients for P/RT series expansion, according to equations (16) and (20) are equal:

$$C_n = C_2 V_p^{n-2} / (n-1). \quad (10)$$

To find the pressure in the chain clusters zone we make the summation of infinite row (9) with coefficients C_n given by the expression (10) and come to:

$$P = RTD_m (1 - C_2/V_p \ln (1-V_p D_m)). \quad (11)$$

From Equations (9) and (11) we come to the Equation for modeled values of density in the chain clusters zone:

$$D = D_m + C_2 D_m^2 (1/ (1-V_p D_m) - \ln (1-V_p D_m) / (V_p D_m)). \quad (12)$$

The system of equations (11-12) forms the parametric Equation of State for chain clusters domination zone [19]. In this zone the precision of prediction $D (P)$ is better than 0.1%.

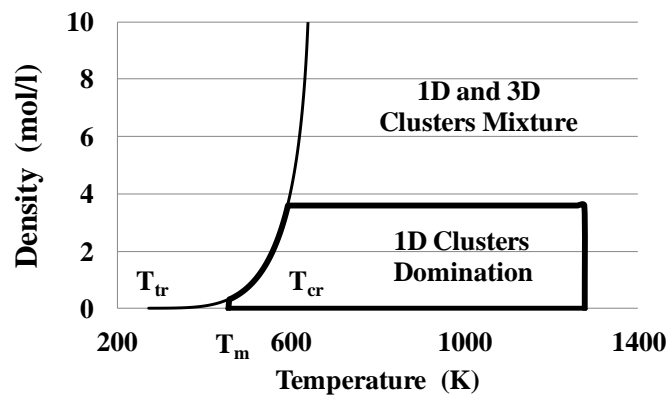


Fig. 10. The chain clusters domination zone in the Water vapor marked by a thick border area, limited by the saturation density curve (thin line) and by one fifth of the critical density at near critical and supercritical T [17,19]

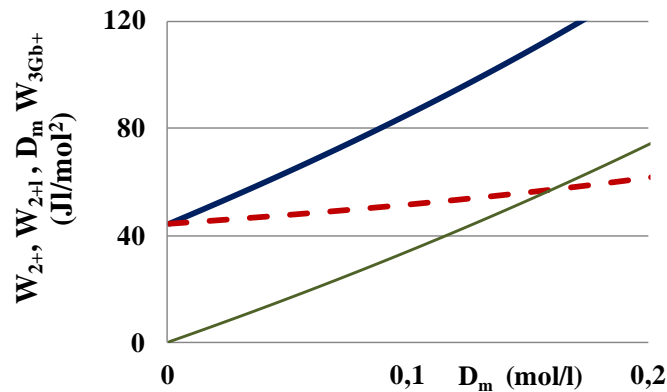


Fig. 11. Comparison of values for the pair bond function W_{2+} , calculated from experimental data for Ne at $T = 24.6$ K (thick line), and its chain models: normal, $W_{2+i} = W_2 / (1 - V_{u2} D_m)$ (dashed line) and abnormal, $D_m W_{3+i} = D_m W_{3G} / (1 - V_{u3} D_m)$ (thin line)

2.6 Chain Clusters in Neon

For Neon at temperatures lower than $T_m = (T_{tr} + T_{cr})/2$ a coexistence of two types of linear Chain clusters had been noticed. The first, normal, type starts from dimers and its pair bond function $W_{2+i} = W_2 / (1 - V_{u2} D_m)$. The second, abnormal, type starts from trimers with giant bond energies and its triple bond function $W_{3g+i} = W_{3g} / (1 - V_{u3} D_m)$. The total pair bond function $W_{2+} = W_{2+i} + D_m W_{3g+i}$.

Values for the pair bond function W_{2+} and W_{2+l} of the normal Chain clusters' complex are shown at the Fig. 11 together with the contribution ($D_m W_{3g+l}$) in the pair bond function W_{2+} of abnormal chain clusters with giant bond energies.

The Fig. 12 demonstrates an excellent coincidence of the real pair bond function W_{2+} and its model:

$$W_{2+mod} = W_{2+l} + D_m W_{3G+l}.$$

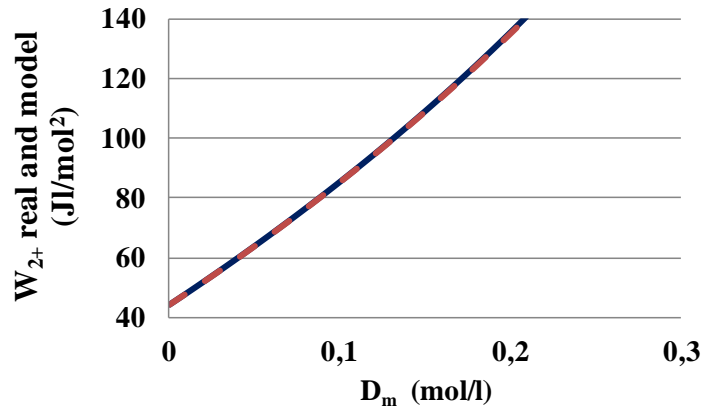


Fig. 12. Coincidence of values for the pair bond function W_{2+} , calculated from experimental data for Ne at $T = 24.6$ K (solid line) and its model as a sum of functions for linear clusters: $W_{2+mod} = W_{2+l} + (D_m W_{3g+l})$ (dashed line).

The bond energy for abnormal giant trimers had been estimated as the tangent of slope of the $\ln(W_{3g})$ versus $1000/T$ graph [18], Fig. 13.

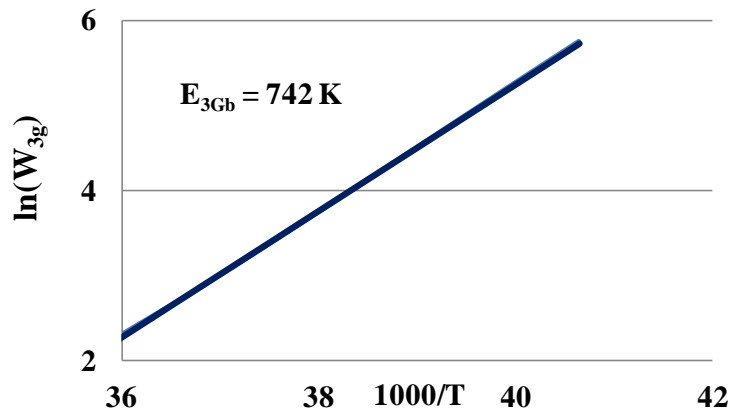


Fig. 13. Estimation of the giant bond energy E_{3g} for a complex of abnormal chain clusters, starting from trimers.

The value of bond energy of abnormal trimers is much larger than the pair interaction energy estimated for the normal dimer fraction in Neon, Fig. 14.

If we compare the giant bond energy for trimers in Neon, shown at Fig. 13, and the pair bond energy, Fig. 14, we can see a huge difference.

The huge difference of bond energies in abnormal and normal chain clusters may be explained by a new type of bonding in abnormal Ne trimers [18] caused by the unknown mechanism of quantum

chemical interactions. This mechanism, once appeared in the original trimer, is transferred to all next bonds in a chain. The Fig. 15 gives a schematic comparison of chain cluster structures for abnormal (upper chain) and normal (lower chain) clusters in Neon.

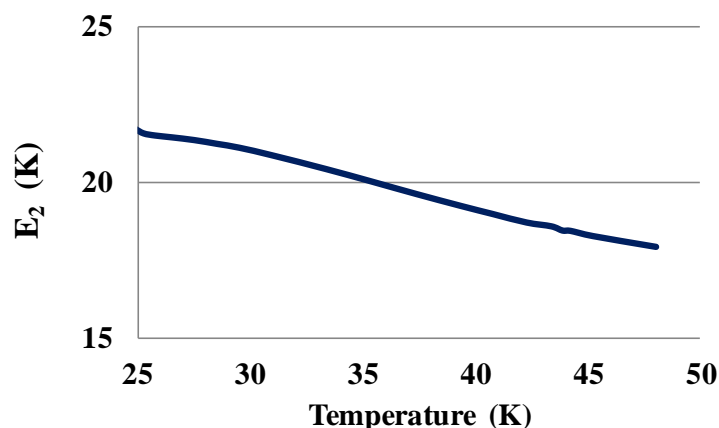


Fig. 14. The temperature dependence $E_2(T)$ of the pair bond energy in the normal chain cluster of Neon

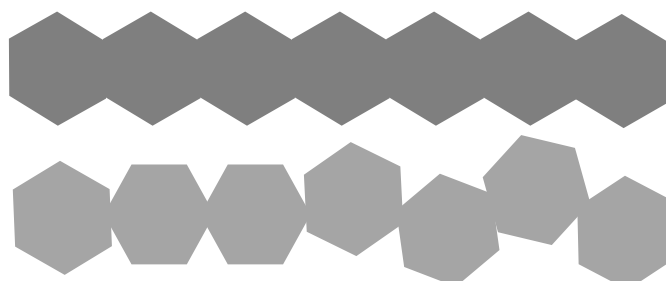


Fig. 15. The abnormal chain cluster in Neon with giant pair bond energies (upper chain) and normal chain cluster (lower chain)

The small bond energy in the normal dimer is transferred to next bonds at the further growth of the chain length as it is. The difference in the chain growth volumes, V_{u2} and V_{u3} , tells in favor of a new mechanism of bonding in abnormal trimers. For example, at $T = 24.6$ K $V_{u2} = 1.42$ l/mol, but in abnormal clusters $V_{u3} = 0.74$ l/mol. Almost double diminishing of the chain growth volume in abnormal clusters may be explained by a stronger orientation of bonds in abnormal chain clusters.

This surprising result confirms once more the idea of the lack of universality in the molecular interaction mechanisms of different pure gases. The coexistence of ordinary physical interactions between atoms in Neon with quantum chemical interactions requires more profound theoretical and experimental investigation.

4. LARGE 3D CLUSTERS' PROPERTIES ESTIMATION

4.1 The Approach to the 3D Clusters' Properties Estimation

At densities over the upper boundary of the chain clusters domination zone and up to the critical density there is a zone of 1D and 3D clusters coexistence. To study the properties of 3D clusters in this zone it is needed to remove from the total potential energy the contribution of chain clusters. The deviation of the graphs at Fig. 6 and 9 from linearity results from the growing contribution of 3D clusters to potential energy at a density over one fifth of the critical density. The knowledge of the

chain clusters' properties permits to extrapolate the chain clusters' contribution to the zone of 1D and 3D clusters mixture [15,16,20]. The difference ΔW_{2+} between W_{2+} and W_{2+i} reflects the contribution of 3D clusters in the potential energy density at near critical pressures, Fig. 16.

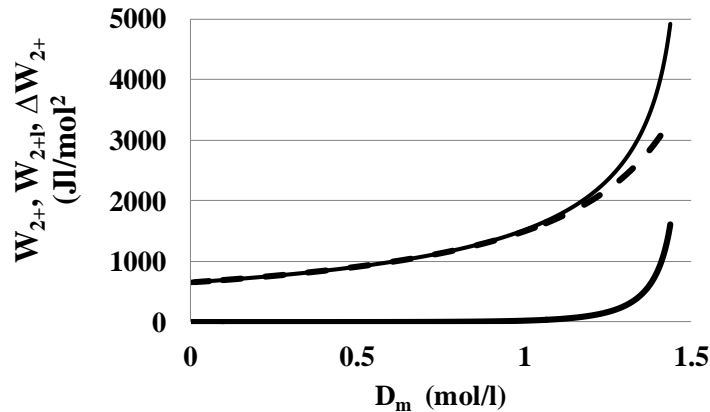


Fig. 16. A difference ΔW_{2+} (thick line) between W_{2+} (thin line) and 1D clusters contribution extrapolation W_{2+i} (dashed line) in Xe at 280 K.

It is due to the growth of both: the 3D clusters population and the averaged number of bonds in 3D clusters. The investigation of equilibrium clusters at near critical densities is very important for technologies, based on supercritical fluids [16,20]. To move forward this practically important direction of research the properties of large clusters should be known in more details.

At the critical temperature in the Water vapor the noticeable growth of the 3D clusters contribution to the gas potential energy starts at 160 bar and steeply grows approaching to the critical pressure, Fig. 17.

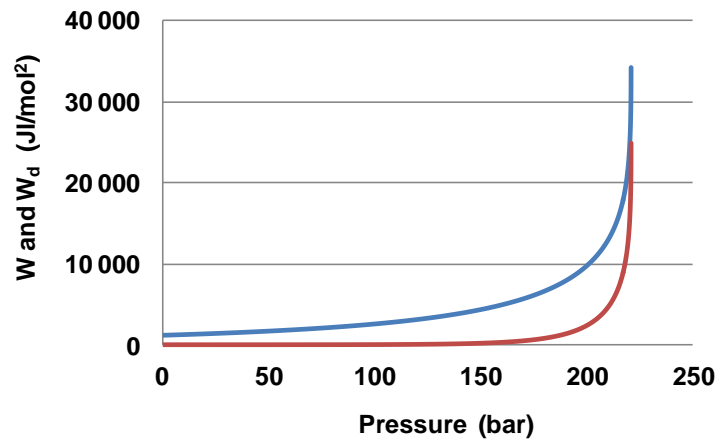


Fig. 17. The comparison of the total potential energy density function W (blue line) and the 3D clusters contribution W_d (red line) in the Water vapor at $T = 647$ K near the critical temperature

4.2 The Averaged Number of Particles in the 3D Clusters

The Fig. 16 shows that the $\Delta W_{2+}(D_m)$ function reflecting the contribution of 3D clusters, becomes noticeable and steeply grows at D_m over 1 mol/l. Instead of the series expansion of this highly nonlinear function we find an averaged number n_{av} of particles in the 3D cluster fraction via differentiation of natural logarithm of ΔW_{2+} by natural logarithm of D_m :

$$n_{av} = \partial \ln (\Delta W_{2+}) / \partial \ln(D_m)|_{\tau}.$$

The result for 3D clusters in Xenon at T = 280 K is shown at the Fig. 18.

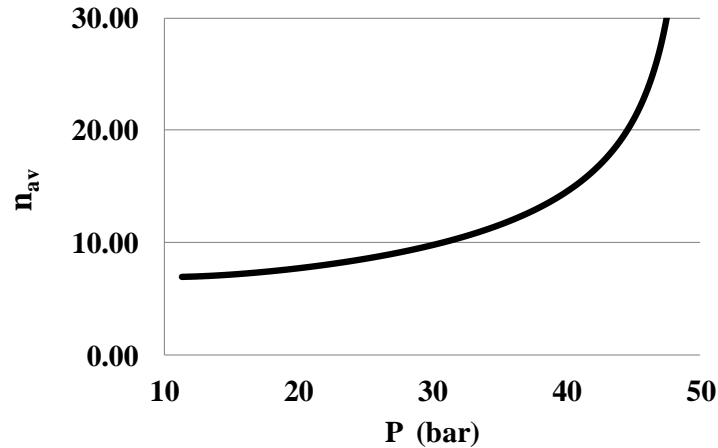


Fig. 18. The pressure dependence of the averaged number, n_{av} , of particles in 3D clusters in Xenon real gas at T = 280 K.

It is seen that in Xenon at a near critical temperature 280 K and at pressures 10-20 bar the averaged number of atoms in 3D clusters is around 7. It might be a central atom, surrounded by 6 outer atoms.

4.3 The Numbers of Particles in Different Dominating 3D Cluster Fractions

It is possible to find the numbers of particles in the dominating 3D cluster fractions step-by-step, removing the contributions in the W_{2+} of already analyzed 3D cluster fractions [16, 20]. Here we repeat our approach with the chain clusters' contribution [5]. The Fig. 19 shows the temperature dependences of the lowest 3D cluster fractions in the Water vapor.

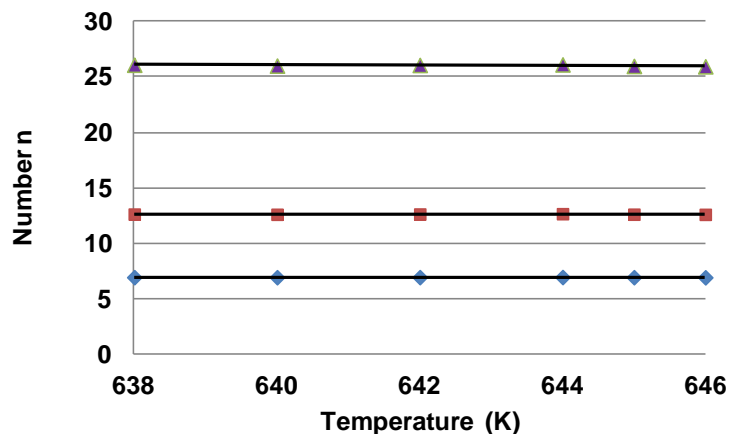


Fig. 19. The numbers of molecules in the first three dominating 3D cluster fractions in the subcritical Water vapor

The Fig. 19 shows that the numbers of molecules in the three lowest dominating cluster fractions are almost independent on temperature in the range 638 - 646 K. It should be noted that the numbers of particles in the first dominating fraction is the same for Xenon and Water vapor and is close to 7.

The next three dominating fractions in the near critical Water vapor are shown at the Fig. 20.

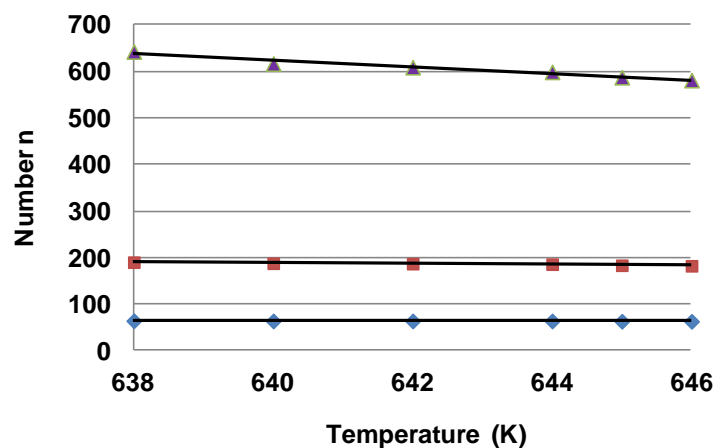


Fig. 20. The numbers of molecules in clusters of the next three dominating fractions in the near critical Water vapor

The Fig. 20 shows that the temperature dependence of the molecules numbers becomes noticeable only for the sixth dominating fraction. The results for higher fractions are not so stable, but reach the 1000 level. So, the knowledge of the chain clusters properties made possible the 3D clusters investigation in near critical fluids, resulted in the discrete structure of dominating numbers discovery.

4. SUMMARY AND CONCLUSIONS

- The monomer fraction density based analysis of precise thermophysical data for pure real gases results in the new class of clusters discovery.
- The canonical expansion of the atomic gases potential energy density by the monomer fraction density provides information about bond parameters in linear chain clusters.
- The inverse function for potential energy density has proven to be the key to inverse problem of linear clusters solving.
- The knowledge of the chain clusters' properties paves the way to large 3D clusters study.
- The knowledge of the large 3D clusters' properties serves for understanding the continuity of the gaseous and liquid states of matter.

COMPETING INTERESTS

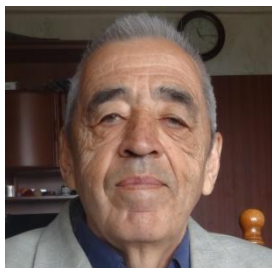
Author has declared that no competing interests exist.

REFERENCES

1. Sedunov B. Monomer fraction in real gases. *Int. J. of Thermodynamics*. 2008;11(1):1-9.
2. Sedunov B. The monomer fraction density based theory of real gases. *JETC book of abstracts Barcelona*. 2019;109.
3. Koudryavtsev AB, Jameson RF, Linert W. *The law of mass action*. Berlin: Springer-Verlag; 2001.
4. NIST. *Thermophysical Properties of Fluid Systems*; 2020. Available:<http://webbook.nist.gov/chemistry/fluid>
5. Sedunov B. The analysis of the equilibrium cluster structure in supercritical carbon dioxide. *American J. of Analytical Chemistry*. 2012;3(12A):899-904. DOI: 10.4236/ajac.2012.312A119
6. Sedunov B. Equilibrium molecular interactions in pure gases. *J. of Thermodynamics*. 2012; 2012:Article ID 859047:13.
7. Sedunov B. *The wonders of molecular interactions*. Saarbrucken, Germany: Lambert Academic Publisher. 2016;98.

8. Aster RC, Borchers B, Thurber C. Parameter estimation and inverse problems, 2nd edn. Elsevier; 2012.
9. Yarris L. Clusters: A new state of matter. Berkeley LAB Publication Archive; 1991. Available:<https://www2.lbl.gov/Science-Articles/Archive/clusters.html> (accessed Dec. 2, 2020).
10. Sedunov B. An advanced platform for thermodynamics education. Part one: Small density pure real gases. *Int. J. of Thermodynamics*. 2020;23(3):224-232. Available:<https://dergipark.org.tr/en/download/article-file/1028840>
11. Sedunov B. Thermodynamics of the pure real gas system. JETC book of abstracts, Barcelona. 2019;72.
12. Feynman R. Statistical mechanics; A set of lectures. W.A. Benjamin, Inc., Massachusetts; 1972.
13. Sedunov B. Thermal analysis of thermophysical data for equilibrium pure fluids. *Journal of Modern Physics*. 2013;4(7B):8-15. DOI: 10.4236/jmp.2013.47A2002.
14. Sedunov B. The Pure Gases' Thermophysical Data Computer Aided Analysis, a book chapter in the: *New Insights into Physical Science*. Book Publisher International, Hooghly, West Bengal, India. 2020;11.
15. Sedunov B. Equilibrium structure of dense gases. Proc. of the JEEP-2013, Nancy, France, MATEC Web of Conferences; 2013. Available:<http://dx.doi.org/10.1051/mateconf/20130301002>
16. Sedunov B. Nanosized objects in equilibrium supercritical fluids. Proc. of the JEEP-2013, Nancy, France: MATEC Web of Conferences, 3, 01062; 2013, DOI:10.1051/mateconf/20130301062
17. Sedunov B. The molecular physics of chain clusters. ATINER's Conference Paper Series PHY2015-1711, Athens, Greece; 2015,
18. Sedunov B. Thermal physics of clusters in atomic gases, a book chapter in the: *Newest Updates in Physical Science Research*, Book Publisher International, Hooghly, West Bengal, India; 2020.
19. Sedunov B. *The discovery of the cluster world*", Saarbrucken, Germany: Lambert Academic Publisher. 2015;102.
20. Sedunov B. Structural transition in supercritical fluids. *Journal of Thermodynamics*. 2011;2011: Article ID 194353:5.

Biography of author(s)



Boris Sedunov

Computer and Information Systems Department, Russian New University, Moscow, Russia.

He was born in 1940 in Eastern Siberia, Russia. He graduated from the Moscow Institute of Physics and Technology, where he studied nuclear, atomic and molecular physics, biophysics and electronics. His PhD thesis was in the solid states physics. He aims to solve the challenging problem of the cluster nature and bond parameters investigation. He managed to extract properties of clusters and molecular interactions basing on precise thermophysical data for pure real gases and their potential energy density. He noticed the fluid basic particles' chemical potential independence on their entrance to different cluster fractions and introduced the monomer fraction density, which has proven to be a perfect argument for canonical cluster expansion, respecting the Mass action law. On this way he has discovered a new class of linear chain clusters, dominating in gases at moderate densities. He has determined a wide zone of densities and temperatures, where these clusters dominate. The extrapolation of their properties to larger densities permitted him to select the large 3-dimensional clusters contribution to the thermophysical properties of super dense gases. This approach has proven to be very useful for understanding the cluster nature transformation at the gas-to-liquid continuous transition in supercritical fluids. His ideas and discoveries are widely published in International scientific journals, reported on conferences and are reflected in two books: *Discovering the Cluster World* and *The Wonders of Molecular Interactions*, published in the Lambert Academic Publishers. His computer aided analysis of precise experimental thermophysical data may be favorable for the advanced thermodynamics education.

© Copyright (2021): Author(s). The licensee is the publisher (B P International).

DISCLAIMER

This chapter is an extended version of the article published by the same author(s) in the following journal. *American Journal of Analytical Chemistry*, 3: 899-904, 2012.