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The Molecular Physics of Chain Clusters

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The Molecular Physics of Chain Clusters

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Abstract

At the 2nd ATINER Conference on Physics the author declared that the physics of clusters in real gases benefits from the computational analysis of the precise data contained in the NIST database for Thermophysical Properties of Fluids. The paper demonstrates the discovered by this way unknown type of chain clusters, existing in many equilibrium pure gases, such as noble and polar gases, CO₂, SO₂, and Alkanes. 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 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 which opens possibilities of investigating the clusters' formation physics. The analysis of the experimental data demonstrates independence on the chain length of the characteristic volume for chain formation. This auto-model feature permits to calculate equilibrium coefficients for a long row of chain clusters with growing numbers of particles. The paper demonstrates temperature dependencies of the chain formation volume for a number of pure gases and their correlation with the equilibrium coefficients for dimer fractions. The geometric progression law for the chain cluster characteristics permits to extrapolate to higher densities the chain clusters' contribute in the potential energy just to exclude it. This procedure opens the way to study 3D clusters at near critical densities.

Keywords: Bond energy, cluster, dimer, equilibrium, molecular interaction, real gas, thermophysical property

Introduction

Numerous material objects around us have been formed by an action of chemical forces and intermolecular interactions during the cooling process of gaseous clouds, which in the young and hot Universe consisted originally mainly of free moving atoms. When temperature in a certain domain of the Universe becomes low enough, the atoms join in molecules, which their lifetime may overcome centuries. For this reason the molecules appear as permanently existing elementary components of matter in this part of the World. If the temperature of this domain keeps falling down, the weak attraction forces between molecules, discussed by Rowlinson (2002), obtain a power to create a plurality of tiny subnanosized and nanosized molecular complexes that give origin to larger material agglomerations, such as the interstellar dust and asteroids at the first step and planets at the next step. By this way the molecular interactions play an important role in the formation of the environment, surrounding people on the Earth. Therefore, the investigations of molecular complexes and the physics of their formation are very important.

In real gases these molecular complexes are presented by clusters, discussed by Feynman (1972) and Mayer and Goeppert-Mayer (1977). The molecular interactions in clusters, argued by Kaplan (2006), are much weaker than the chemical forces, but this weakness is compensated in clusters by much larger, than in molecules, volumes of attraction zones, whose values had been estimated in the works of Sedunov (2012a; 2013a). A greatly enlarged, as compared to chemical bonding, attraction zone volume raises probability of clusters formation, especially at high densities of gases, in spite of small intermolecular bond energy. The clusters' bond energies are of the same order of magnitude as the energies of thermal movement. It makes the spectral analysis ineffective for equilibrium clusters investigation, while for chemical compounds it has proven to be very informative.

So, there is a need in alternative methods of cluster characteristics investigation. At the 2nd ATINER Conference on Physics Sedunov (2014) demonstrated that the physics of equilibrium clusters in real gases can be based on the computational analysis of precise thermophysical data from the NIST database for Thermophysical Properties of Fluids, the Webbook.NIST (2011). The clusters strongly influence the thermophysical properties of the real gases. The computational analysis of the precise thermophysical data from the NIST database, developed by Sedunov (2012a), provided initially the knowledge of the cluster bond parameters only at low densities of real gases.

For larger densities D and pressures P Sedunov (2012b; 2013b) has suggested an application of the geometric progression law to a particular class of clusters, namely the 1D chain clusters discovered in many gases such as noble and polar gases, CO_2 , SO_2 , and Alkanes. To analyze the properties of chain clusters a special mathematical method had been developed and the zones of temperatures and densities, where they dominate over 3D clusters, were determined. The analysis shows independence on the chain length of the characteristic volume, responsible for the chain growth. The product of this

volume by the monomer fraction density is a common ratio of the geometric progression law for a row of chain clusters with growing numbers of particles. The geometric progression law permits to extrapolate the chain clusters' contribution in the total potential energy to near critical density. By this way we can separate the 3D clusters' contribution from the 1D clusters' contribution. It opens the possibility to investigate the 3D equilibrium clusters at high densities of gases.

The goal of this paper is to demonstrate wide temperature-density zones in a number of gases, where the chain clusters can dominate, the characteristics of 1D chain clusters and the first results of the 3D clusters investigation.

The Discovery of Chain Clusters

A Novel Approach to the Experimental Data Processing

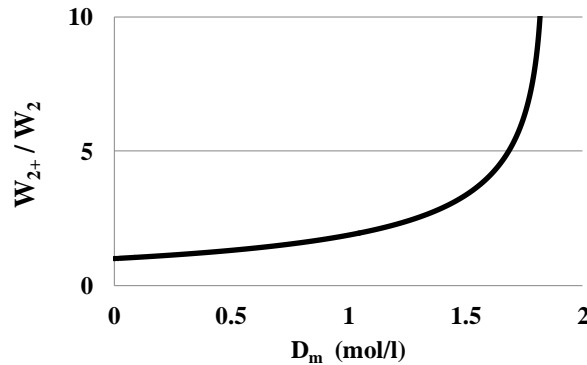
The thermal analysis of regularized experimental thermophysical data method, developed by Sedunov (2012a; 2013a), provides a physically clear vision of the cluster fractions' structure in pure real gases. The method is based on the series expansion of equilibrium thermophysical functions by the monomer fraction density D_m , introduced by Sedunov (2008). The method is related to the so called inverse mathematical problem arising in the processes of hidden parameters extraction from experimental data and for this reason is very sensitive to errors in the experimental data. But the utilization of the regularized data from the Webbook.NIST (2011) database permits to solve the problem successfully.

The most informative thermophysical function for this analysis happened to be the potential energy $U = (E(T, P) - E(T, 0))$, 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 be expanded by D_m . The zero pressure limit of it gives the pair interaction coefficient W_2 of the potential energy density.

The Discovery of Chain Clusters in Real Gases

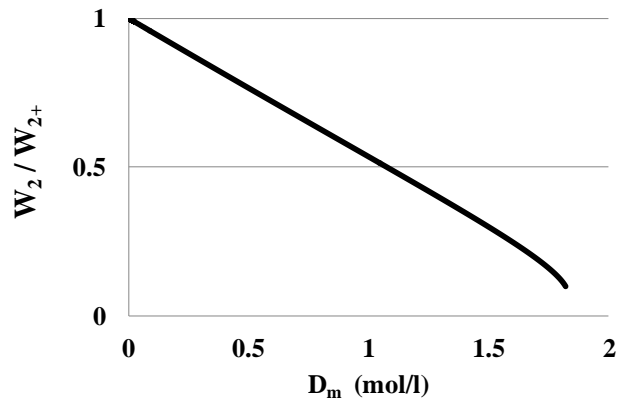
The first authors' attempts to extract the clusters' bond parameters brought reliable results only for small clusters with numbers of particles from two to four. For growing numbers of particles in clusters the results were less reliable. But in the case of Carbon Dioxide Sedunov (2012b) made a breakthrough to larger clusters at an attempt to expand in a series by D_m a highly nonlinear W_{2+} / W_2 function, shown at the Figure 1.

Figure 1. *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*



The author noticed that the inversely proportional function W_2 / W_{2+} , shown at the Figure 2, keeps a wonderful linearity in a wide range of D_m , up to 1.4 mol/l. In Carbon Dioxide the upper boundary of this range corresponds to large values for pressure, $P = 45$ bar, and gas density, $D = 2.4$ mol/l. The plot for the inverse ratio, W_2 / W_{2+} , shown in Figure 2, demonstrates linearity in a wide range of the monomer fraction density. This linearity opens the way to investigation of equilibrium clusters at large pressures and densities of a real gas.





Figure 2. *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 45 bar*



A linear part of the graph in Figure 2, with V_u being the tangent of the 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 $V_u D_m$. This law tells that an attachment of the next monomer to the n -particle cluster has a universal mechanism for all numbers n . The only explanation of this remarkable fact is the 1D chain type of clusters, Table 1, which has the same

bond energy E_2 for all bonds in a chain and a universal mechanism of the chain length growth.

Table 1. *The 1D Polymer-like Chain Clusters and the Geometric Progression Law for their Equilibrium Coefficients*

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	$2E_2$	$3E_2$	$(n-1)E_2$

The Geometric Progression Law for Chain Clusters in Different Gases

An indication on the geometric progression, the linearity of the W_2 to W_{2+} ratio dependence on D_m , had been noticed for many investigated pure gases. The W_2 / W_{2+} versus D_m dependence in SO_2 , was investigated in the zone of T between 325 and 525 K and pressures up to 8 bar. The perfect linearity of the diagrams for the temperatures 325 and 525 K, seen from in Figure 3, confirms a domination of the chain clusters in this zone of temperatures and pressures.

Figure 3. *The W_2 to W_{2+} Ratio Linear Dependence on D_m in SO_2 for Pressures up to 8 bar, at $T = 325$ K (Thick Line) and 525 K (Thin Line), Demonstrating a Domination of Chain Clusters in this Zone*

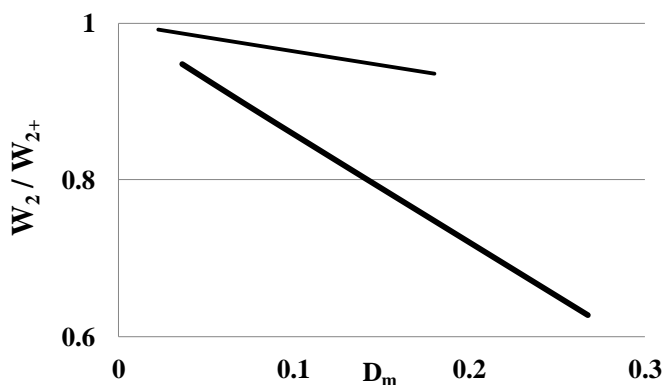
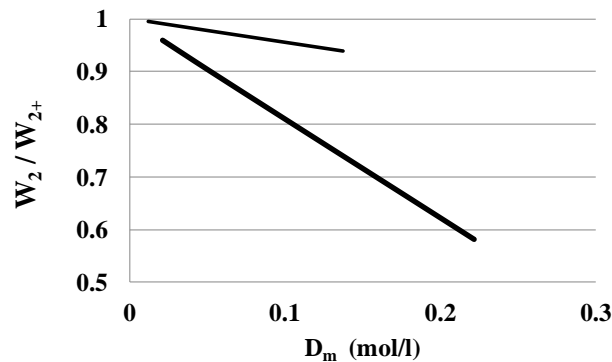


Figure 3 results from the isobaric data analysis. The maximal value for pressure in this case was limited by the saturation pressure at $T = 325$ K. In the isothermal data analysis it is possible to select different maximal values of pressure for different temperatures. The analysis at high pressures gives the boundary of the 1D clusters zone, beyond which the contribution of 3D clusters becomes noticeable and the domination of 1D chain clusters finishes.

A similar picture is seen for Hydrocarbons. In Propane the W_2 to W_{2+} ratio linearly depends on D_m at T between 280 and 500 K and P up to 5.8 bars (Figure 4).

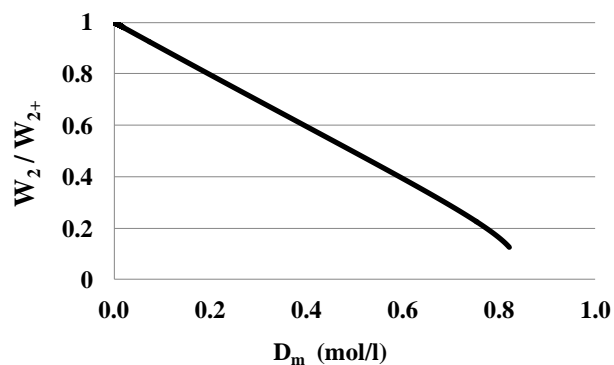
Figure 4. *The Linear W_2 to W_{2+} Ratio Dependence on D_m Demonstrating Correspondence of the Chain Clusters in Propane to the Geometric Progression Law at P from 0 to 5.8 bar; $T = 280$ K (Thick Line) and 500 K (Thin Line).*



The maximal value for pressure in this case had been also selected not from conditions of linearity, but as the saturation pressure at $T = 280$ K.

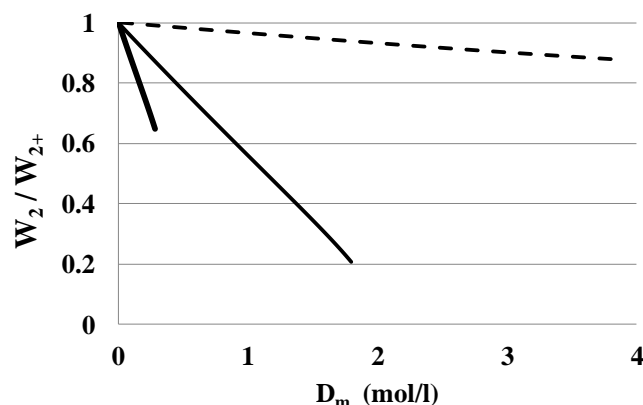
In Propane at $T = 360$ K, in an enlarged range of pressures, the deviation, seen at Figure 5, from the W_2 / W_{2+} versus D_m linear dependence starts at $D_m = 0.6$ mol/l. It corresponds to the total density near 1 mol/l. The maximal pressure is four times higher than in the previous case and the maximal density of the linearity range approximately equals to one fifth of the critical density.

Figure 5. *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.*



Also in the Water vapors the maximal density of the linearity range for the W_2 / W_{2+} dependence on D_m falls approximately at one fifth of the critical density. The dependences taken at 460, 600 and 1200 K, presented at the Figure 6, demonstrate a wonderful linearity in wide ranges of pressures and densities.

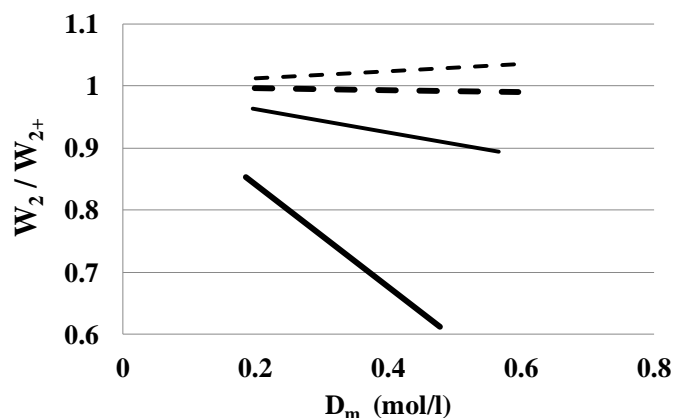
Figure 6. The W_2 to W_{2+} Ratio Dependences on D_m in Water at $T = 460$ (Thick Line), 600 (Thin Line) and 1200 K (Dashed Line)



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 the slope. That means that the chain growth characteristic volume strongly depends on temperature. This dependence is also seen at the Figure 7 for Krypton.

In the Noble gases the zone of 1D chain clusters domination also is wide. The analysis of the 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 (Figure 7).

Figure 7. 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)



So, clusters in many dense gases show universal behavior in the zone, where the W_2 to W_{2+} ratio linearly depends on the monomer fraction density, D_m . 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 a series expansion of thermophysical values.

The linear parts of the graphs for W_2 / W_{2+1} in Figures 2-7 correspond to the law:

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

The W_{2+1} / W_2 function is inversely proportional to the W_2 / W_{2+1} function, expressed by equation (1), and as a sum of geometric progression corresponds to the equation (2):

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

The common ratio of the geometric progression, $V_u D_m$, in the zone of chain clusters domination is smaller than 1. Therefore, the contribution of long clusters in the total potential energy quickly falls with their length. And practically the row of chain clusters may be limited by a number of particles in the longest cluster without noticeable errors in the estimation of the total potential energy. A simple form of the expression (2) opens a wonderful possibility to investigate the new class of clusters with this remarkable behavior, occupying a very wide temperature-density zone.

The Properties of Chain Clusters

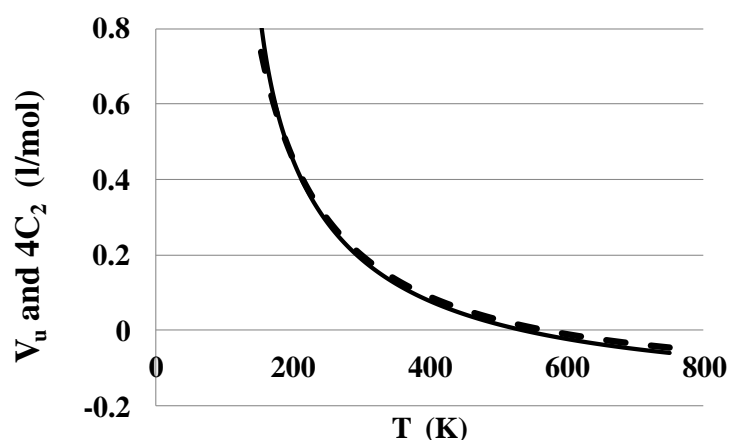
Correlation of the Chain Growth Characteristic Volume and the Pair Interaction Coefficient for Pressure-Density Relations

The temperature dependence of the chain growth characteristic volume V_u in Krypton has proven to be very close to the temperature dependence for the function $4 C_2(T)$ (Figure 8). Here $C_2(T)$ is the pair interaction coefficient for the system of series expansions of pressure and density by D_m :

$$\begin{aligned} P &= RT \sum C_n D_m^n, \\ D &= \sum n C_n D_m^n, \\ C_1 &= 1. \end{aligned}$$

This system of equations was derived by Sedunov (2008) and confirmed for many real gases. A pretty good correlation of $V_u(T)$ and $4C_2(T)$ was noticed for all investigated gases.

Figure 8. *The Correlation of V_u (Solid Line) and $4C_2$ (Dashed Line) in Krypton, Reflecting the Sign Change for Both Functions near the Boyle Temperature*

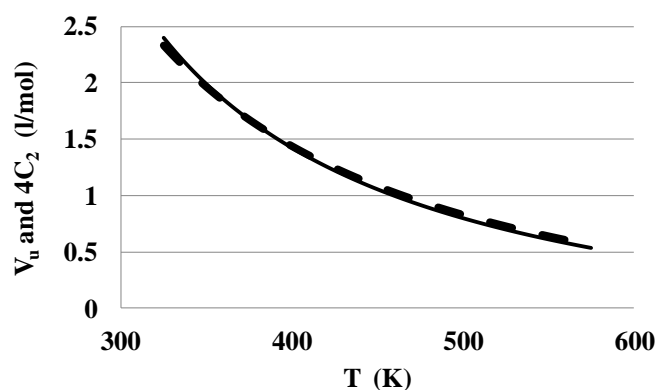


It is interesting to note that near $T = 500$ K the tangent of the slope for the W_2 / W_{2+} graph in Krypton changes its sign. At temperatures over the Boyle temperature the contribution to W_n of monomers' elastic collisions with (n-1)-particle chain clusters makes $V_u(T)$ negative, quite similarly with the change of sign in $C_2(T)$.

This correlation shows that the new particle attachment to a chain cluster is governed by the same mechanism as the mechanism of the dimers formation from monomers. As it was shown by Sedunov (2008), the pressure in real gas is sensitive not only to real physical dimers, but also to virtual dimers, formed in elastic collisions of two monomers. Therefore, the series expansion coefficient W_n is related not only to the n-particle chain cluster fraction, but also to the smaller length chain clusters colliding with the monomers.

A similar picture reflects the correlation between the chain growth characteristic volume $V_u(T)$ and $4C_2(T)$ in Butane (Figure 9).

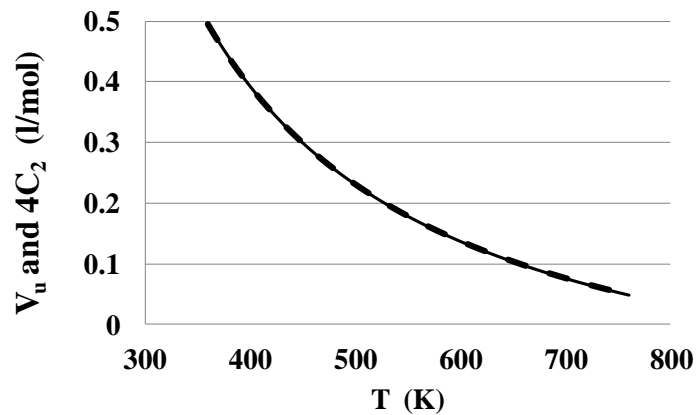
Figure 9. *Correlation of the Chain Growth characteristic volume V_u (Solid Line) and $4C_2$ (Dashed Line) in Butane at Pressures up to 5 bar*



For Butane the upper limit of temperatures in the NIST database was lower than the Boyle temperature. So, both functions in this case stay positive.

A slight difference between $V_u(T)$ and $4C_2(T)$ had been noticed for many investigated gases and needs to be studied more carefully. It is quite natural to see the influence of the cluster particles included in a chain on the conditions for attachment of a new particle to the chain. So, in general, the conditions for the dimer formation are not exactly the same as the conditions for the third particle attachment to the previously formed dimer. But in H_2S the two graphs almost coincide in a wide range of T from 360 to 760 K, Figure 10.

Figure 10. *The Coincidence of V_u (Solid Line) and $4C_2$ (Dashed Line) in H_2S*



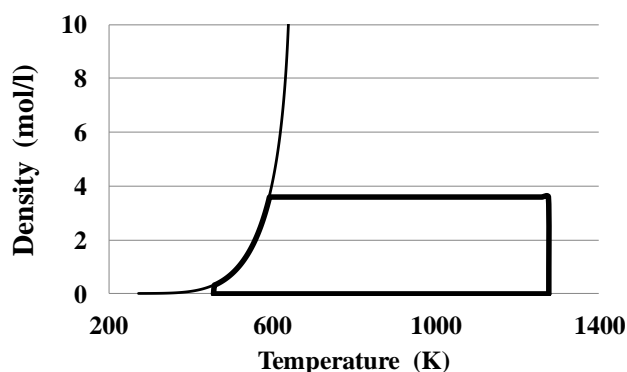
The Zone of Chain Clusters Domination

The analysis of the experimental data for many gases 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,

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

in a wide range of densities D , up to one fifth of the critical density D_{cr} , Figure 10. At $T < T_m$ the saturation density is so small that the presence of clusters with $n > 4$ cannot be noticed. So, at these temperatures it is useless to discuss the row of chain clusters. Moreover, in this range, in spite of low saturation density, the 3D tetramer clusters have been seen in the Water vapor due to huge values for their equilibrium constants at low temperatures. In Figure 11 the zone of the 1D chain clusters domination in the Water vapor is depicted.

Figure 11. *The Chain Clusters Domination Zone in the Water Vapor Marked by the 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*



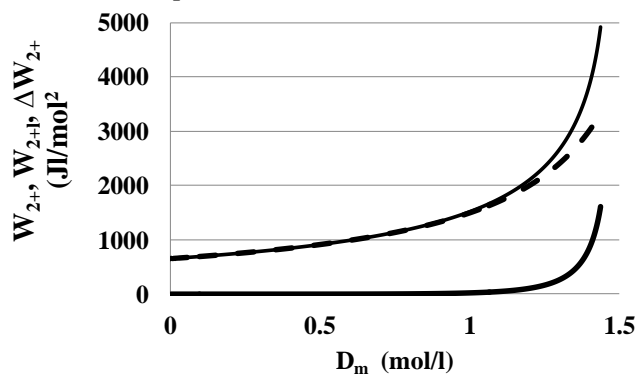
The linearity of the W_{2+1} function, discovered for many investigated dense gases, shows the existence of an infinite row of 1D, polymer like, chain clusters in the zone of their domination.

3D Clusters' Properties Estimation

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 coexistence for the 1D and 3D clusters. To study the properties of the 3D clusters in this zone the removal of the contribution of chain clusters from the total potential energy is necessary. The knowledge of the chain clusters' properties permits to extrapolate the chain clusters' contribution (2) to the zone of the 1D and 3D clusters coexistence. The difference ΔW_{2+} between W_{2+} and W_{2+1} reflects the contribution of the 3D clusters in the potential energy density at near critical pressures (Figure 12).

Figure 12. *A Difference ΔW_{2+} (Thick Line) between W_{2+} (Thin Line) and 1D Clusters Contribution Extrapolation W_{2+1} (Dashed Line) in Xe at 280 K*



The deviation of the graphs in Figures 2, 5 from linearity at D_m over the one fifth of the critical density results from the growing contribution of the 3D clusters. This growth is connected with the growth of the 3D clusters population and with the growth of the number of particles in the 3D clusters.

The investigation of equilibrium clusters at near critical densities is very important for technologies, based on supercritical fluids. Sedunov (2013c) has developed mathematical models for the solubility of condensed substances and the diffusivity in supercritical fluids based on the characteristics of cluster fractions. To move beyond this practically important direction of research the properties of clusters should be known in more details.

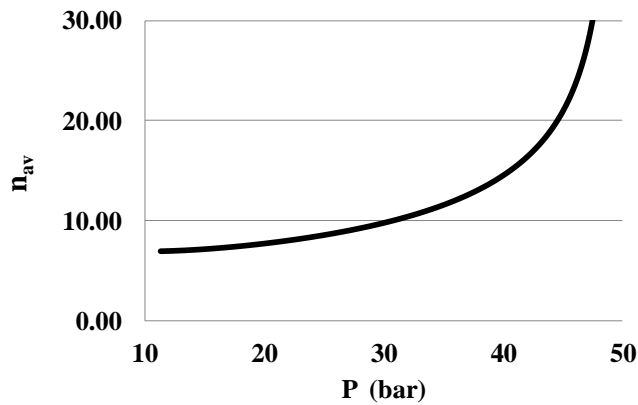
The Averaged Number of Particles in the 3D Clusters Fraction Estimation

Figure 12 shows that the $\Delta W_{2+}(D_m)$ function, which reflects the contribution of the 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 the differentiation of the natural logarithm of ΔW_{2+} by the natural logarithm of D_m :

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

The result for the 3D clusters in Xenon at $T = 280$ K is shown at the Figure 13.

Figure 13. A Pressure Dependence of the Averaged Number, n_{av} , of Particles in 3D Clusters in Xenon Real Gas at $T = 280$ K



It is evident that at pressures of 10-20 bar the average number of atoms in the 3D clusters in Xe at a near critical temperature of 280 K is around 7. It might be a central atom, surrounded by 6 outer atoms. At a near critical pressure of 50 bar the averaged number of atoms in 3D clusters in Xe at 280 K grows to 30.

Conclusions

- The interpretation of the equilibrium thermophysical properties of gases in terms of clusters is very productive.
- The monomer fraction density based series expansion of thermophysical values for dense gases discovers properties of 1D chain clusters.
- The temperature-density zone, where the 1D polymer-like chain clusters dominate, is very wide and important for science and practice.
- The characteristics of chain clusters obey to the geometric progression.
- The knowledge of the chain clusters' potential energy opens the way to the 3D clusters investigation.

Nomenclature

- D Total molar density of a real gas, mol/l
- D_m Monomer fraction density, mol/l
- T Equilibrium temperature, K
- T_{tr} Triple point temperature, K
- T_{cr} Critical point temperature, K
- T_m Middle point between triple and critical temperatures, K
- P Pressure, bar
- R Universal gas constant, $J/(mol K)$
- $E(T, P)$ Molar Internal energy of a real gas, J/mol
- U Molar potential energy of a gas, J/mol
- W Positive potential energy density ($-UD$), J/l
- W_2 Pair interaction coefficient, J/mol^2
- W_{2+} Pair interaction function (W/D_m^2), J/mol^2
- W_{2+1} Linear part of the Pair interaction function, J/mol^2
- n Number of particles in the cluster and the order of the series expansion term
- n_{av} Averaged number of particles in the 3D cluster
- E_n n-particle cluster bond energy, K
- E_2 Dimer's bond energy, K
- $C_2(T)$ Pair interaction coefficient for pressure-density relations (l/mol)
- V_u Universal chain growth characteristic volume, (l/mol)

References

- Feynman, R. (1972) *Statistical mechanics. A set of lectures*, Massachusetts: W.A. Benjamin, Inc.
- Kaplan, I. G. (2006) *Intermolecular Interactions: Physical Picture, Computational Methods and Model Potentials*, Hoboken, NJ: John Wiley & Sons.
- Mayer, J. E. and Goeppert-Mayer, M. (1977) *Statistical Mechanics*, 2nd Ed. New York: John Wiley & Sons.

- Rowlinson, J. S. (2002) *Cohesion: A Scientific History of Intermolecular Forces*, Cambridge University Press, Cambridge.
- Sedunov, B. (2008) Monomer fraction in real gases. *Int. J. of Thermodynamics*, 11(1) 1-9.
- Sedunov, B. (2012a) Equilibrium molecular interactions in pure gases. *J. of Thermodynamics*, [Online] Available from: <http://bit.ly/1MUiKWz> [Accessed: 14th April 2015].
- Sedunov, B. (2012b) The Analysis of the Equilibrium Cluster Structure in Supercritical Carbon Dioxide, *American J. of Analytical Chemistry*, 3 (12A) p. 899-904.
- Sedunov, B. (2013a) Thermal Analysis of Thermophysical Data for Equilibrium Pure Fluids, *J. of Modern Physics, Special issue: Thermal Analysis Methods*, 4, 8-15.
- Sedunov, B. (2013b) Equilibrium Structure of Dense Gases, *Proc. of the JEEP-2013, Nancy*, MATEC Web of Conferences [Online] Available from: <http://bit.ly/1OeExf9> [Accessed: 16th June 2014].
- Sedunov, B. (2013c) The Equilibrium Thermal Physics of Supercritical Fluids, *Int. J. of Analytical Mass Spectrometry and Chromatography*, 1, 103-108.
- Sedunov, B. (2014) The Physics of Clusters in Real Gases, ATINER's Conference Paper Series PHY2014-1280.
- Webbook.NIST (2011) Thermophysical Properties of Fluid Systems. [Online] Available from: <http://webbook.nist.gov/chemistry/fluids> [Accessed: 13th April 2015].