The Cluster Physics Chapter for Thermodynamics Education

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Abstract: Thermodynamics education is not easy both for students and teachers. But the Entropy, Chemical potential, Real gas structure, Fugacity, Molecular interaction, Supercritical phenomena chapters become more comprehensible, if introduced via the pure real gases' cluster physics chapter. A pure gas consists of the only one type of basic particles, therefore, the molar Gibbs energy G is universal for all basic particles. The monomer fraction Gibbs energy Gm logarithmically depends on the monomer fraction density, Dm, which is a perfect argument for thermophysical properties series expansions, named canonical for their correspondence to the fundamental Mass action law. Unlike virial expansions, the n-th canonical expansion coefficient reflects properties of the n-particle cluster. The canonical expansion of various thermodynamics functions, for which precise experimental data may be taken from the NIST Webbook, opens the clusters vision from different points of view. The potential energy of a gas provides the clusters' bond parameters cognition. The bond energy temperature dependence discovers different cluster isomers and the directional bonding. The near critical cluster fractions structure reflects the gas-to-liquid soft structural transition. For students it is useful to develop the canonical series expansion and the cluster structure analysis skills.

Keywords: Computer aided analysis, Pure real gas, Bond energy, Cluster, Molecular interaction

> *Today's scientists have substituted mathematics for experiments,*
> *and they wander off through equation after equation,*
> *and eventually build a structure,*
> *which has no relation to reality.*
>
> *Nikola Tesla*

Introduction

It is well known that the thermodynamics is difficult both for students and teachers mainly because of the experimental basis weaknesses. For this reason, some thermodynamics notions stay abstract and seem to be artificial. But such sophisticated notions, as Entropy, Chemical potential, Real gas structure, Fugacity, Molecular interaction, Supercritical phenomena become better comprehensible, if teachers introduce them via the pure gases cluster physics basing on the precise experimental thermophysical data. The pure real gas

platform, based on experiment, is favorable for an advanced thermodynamics education (Sedunov 2020).

A pure real gas is the nearest extension of the widely used in education ideal gas model. Unlike the ideal gas, it includes the molecular interactions, which are the basis of multiple to be studied thermodynamics functions, possessing the largest experimental base. The pure real gas helps to discover the clusters' bond energies.

Unique Features of Pure Real Gases

The cluster physics has a solid experimental basis: many pure real gases have precise databases of their thermophysical properties, like the NIST Webbook (NIST 2021). The pure gases contain only one basic particles type, and for this reason their molar Gibbs energy G is universal for all basic particles (Sedunov 2008), Figure 1. The basic particles of a fluid are particles corresponding to its chemical nature, independently on the cluster structure. The monomer fraction molar Gibbs energy G_m reflects the monomer fraction density, D_m (Sedunov 2008). For an atomic gas $G_m = RT \ln(D_m V_q)$. D_m is a perfect argument for the neat gases thermophysical properties series expansions, named canonical for their correspondence to the fundamental Mass action law (Koudryavtsev 2001). V_q is the basic particles' quantum volume (Kittel 1969).
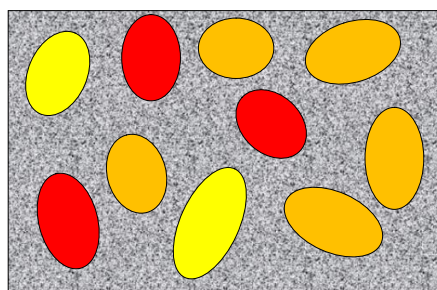

Figure 1. Different clusters (colored figures) in the infinite monomer fraction zone (grey texture) with uniform monomer's density and Gibbs energy (chemical potential).

The monomer fraction zone is filled by uniform density monomers, providing uniform chemical potential. This uniformity results from the chemical equilibrium in the infinite zone. Monomers penetrate in the cluster zones, delivering there the unique chemical potential. In the gas-to-liquid transition at a supercritical temperature we see the reverse picture: liquid fills the infinite cluster zone and monomers fill the pores, Figure 2.
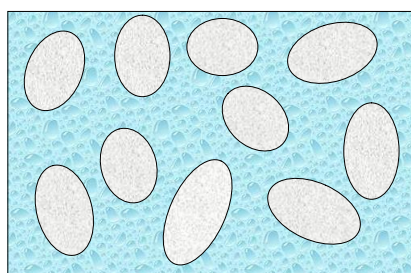

Figure 2. The pores (grey figures) filled with uniform density and unique chemical potential monomers; liquid (blue texture) fills the infinite cluster zone at supercritical temperature and density.

So, the cluster physics explains the Supercritical gas-to-liquid transition!

A very cognitive is the expression for the neat atomic real gas Entropy S (Sedunov 2008): $S = H/T - R \ln(D_m V_q)$, where H is the molar enthalpy, T - temperature, R - Universal gas constant; $V_q = h^3 N_A^4 /(2\pi MRT)^{3/2}$ is the molar quantum volume (Kittel 1969) proportional to the cube of the thermal de Broglie wavelength; h is the Plank's constant, M is the basic particles' molecular mass in kg/mol, N_A is the Avogadro number. This expression extends the Sackur-Tetrode (Sackur 1912), (Tetrode 1912) equation to real atomic gases. For students it is useful to know that this expression differs from the Sackur-Tetrode equation by H/T instead of 2.5R and $1/D_m$ instead of the molar volume V.

The canonical against virial extension

Unlike virial expansion (Mayer 1977) for pressure - density interdependence, the canonical one is valid for any thermodynamics function, providing the vision of clusters from different points of view. The *n*-th canonical expansion coefficient reflects properties of the *n*-particle cluster, but for virial expansions this option was only silently supposed (Feynman 1972). Finally, this hypothesis has proven to be wrong, because the argument for virial expansions, the total density D, is the mixture of partial cluster densities and the *n*-th virial expansion coefficient has proven to be the mixture of contributions from clusters with different numbers of particles.

Clusters now are considered as a new state of matter (Yarris 1991). This idea seems to be inspired by the Mayer's substitution of the Boltzmann factor exp(-E/kT) on the nonphysical factor (exp(-E/kT) - 1) for clusters and by the virial expansion, which is perfect only for raw experimental data generalization, but in application to clusters ignores the Mass action law. The cluster physics seemed to be so strange, that the specialists in thermodynamics had to agree with these violations of the thermodynamics laws. The contemporary chapters on real gases in almost all thermodynamics manuals contain these wrong statements. The goal of this paper is to build the cluster physics respecting fundamental thermodynamics laws and, on this basis, to find understandable explanations for a number of sophisticated notions.

The Cluster Physics Educational Basis

The working data table creation and extension

We suggest to start the pure real gases cluster physics study after studying the General thermodynamics and the Ideal gas model. The initial experimental data for the computer aided thermophysical data analysis may be downloaded from the US National Institute of Standardization and Technology (NIST) Webbook (NIST 2021). The Webbook permits downloading up to 600 lines of the data table at a time. If a higher data precision is needed, it is possible to download the next part of the table, with a possible change of the step. The most usable data table type is an isothermal with a pressure as a leading column and near zero initial pressure. The isobaric

or isochoric versions are also possible. It is a good training for students to create the working data tables.

After the basic data table creation, we add some columns: the $D_p = P/RT$, D_m, $C_{2+} = (D - D_p)/D_m^2$, $W_{2+} = W/D_m^2$. The zero pressure limit of the C_{2+} gives us the second canonical coefficient C_2 for pressure-density-temperature (PDT) relations, which equals to minus B - the second virial coefficient. Only on the second level we see a correlation of virial and canonical coefficients. The coefficients at higher levels differ enormously.

The clusters' bond energies computation method

The potential energy U of a gas, for which precise experimental data may be taken from the NIST Webbook, provides the clusters' bond parameters cognition (Sedunov 2012). We compute the U values as the difference between the Internal energy Eat a current pressure and at zero pressure: $U = E(T, P) - E(T, 0)$. Then we expand in a series the positive potential energy density $W = - UD$, starting from a function $W_{2+} = W/D_m^2$. The zero-pressure limit W_2 of this function is the second canonical coefficient for the potential energy density W. When the W_2 is found we can find the W_3 and so on. The temperature dependences for canonical expansion coefficients W_n provide the *n*-particle cluster bond energies E_n knowledge as the W_n tangents of logarithm dependence on the reverse temperature $\beta = 1000/T$,

The bond energies temperature dependences E_n (T) show different cluster isomers (Sedunov 2013) and the atoms with directional bonding. The possibility to find clusters' bond energies and their temperature dependences is the great advantage of the canonical cluster expansion. The change of the E_n values in some range of temperatures means the soft structural transition between isomers of the n-particle cluster fraction. The larger is the cluster's bond energy, the smaller is the transition zone between stable values for E_n. The near critical cluster fractions' bond energies and structure reflect the gas-to-liquid soft structural transition (Sedunov 2013, March). For students it is cognitive to see the difference between the abrupt phase transition in macroscopic systems and the soft structural transition in small systems, like clusters.

The reverse analytical extension method

To extract properties of clusters from experimental thermophysical data it is needed to solve the inverse mathematical problem (Aster 2012), which requires special measures to diminish the input data and processing errors influence on final results (Hoover 1991). For this goal the computer aided analysis should be interactive. The interactive regime permits to change and adjust the processing algorithms to improve the final precision. The input data errors diminishing task is effectively performed by NIST (Frenkel 2012). But a great part of this job is left to researchers, teachers and students, who have to select the best algorithms for their analysis. It is useful for students to develop the canonical series expansion and the cluster structure analysis skills.

Finding the W_n or C_n coefficients requires a high precision of the $W_{(n-1)}$ or $C_{(n-1)}$ determination. For example, a

small error in C_2 for Neon results in large errors in initial values for C_{3+}, found as $C_{3+} = (C_{2+} - C_2)/D_m$. The C_2 errors mainly influence on the first C_{3+} values. The more is D_m, the lower are the errors in C_{3+}. To diminish the initial errors in C_{3+}, we use the reverse analytical extension method. We compute the corrected initial values $V(D_{m1})$ basing on the values $V(D_{mi})$ for large arguments D_{mi}: $V(D_{m1}) = 3(V(D_{m(1+k)}) - V(D_{m(1+2k)})) + V(D_{m(1+3k)})$. So, from three values $V(D_{mi})$ spaced on k steps we find the initial value $V(D_{m1})$. For $V(D_{m2})$ we shift our three values on one step forward: $V(D_{m2}) = 3(V(D_{m(2+k)}) - V(D_{m(2+2k)})) + V(D_{m(2+3k)})$. And so on.

The Figure 3 shows the correction of the C_{3+} for Neon at T = 70K by the reverse analytical extension method with k = 32. We see that the corrected line has lower curvature and smoothly joins the initial line after k steps. To apply this method we should use the interactional analysis. In this analysis we estimate the needed value for k and see, if 3k does not fall in the zone of the initial line new curvature. In other words, we select the k value in such a way that three shifted arguments should be in the most stable part of the initial line.
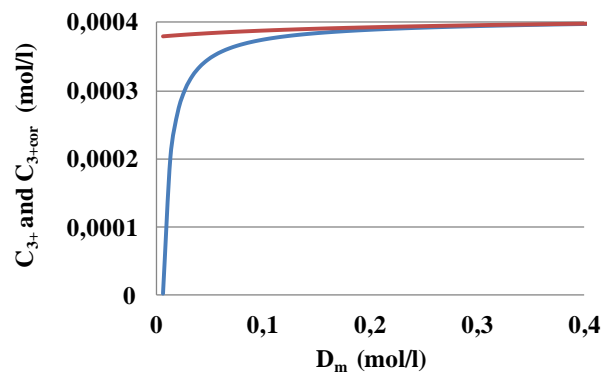

Figure 3. Large errors in the initial C_{3+} values (blue line), corrected by the reverse analytical extension method: corrected values C_{3+cor} (red line).

The reverse extension means that we extend the high stability of the analysis results reached at high arguments to the zone of small arguments, where the errors are most probable. This method is frequently used in our analysis, because the initial parts of curves to be analyzed possess large errors. These errors may be caused by the data discretization, by errors in experimental data, by the data processing. So, the initial parts of curves need a special attention, including the reverse analytical extension method and interactive analysis. These methods may be used by teachers and students.

The Monomer fraction density and Fugacity

To find the monomer fraction density D_m we should solve the differential equation (Sedunov 2008):

$$\partial D_m / \partial P \mid_T = D_m/(RTD). \tag{1}$$

This equation coincides with the equation for Fugacity f: $\partial f / \partial P \mid_T = f /(RTD)$ (Lewis 2001).   It   shows   that

the Fugacity in a pure real gas is the monomer fraction partial pressure f = RTD_m. The Monomer fraction density is a quite clear notion both for teachers and learners and the fugacity definition on its basis has a clear sense. So, the pure real gases physics gives a clear definition to a sophisticated notion Fugacity!

But the traditional definitions for fugacity are rather vague. Lewis gives fugacity (Lewis 2001) a vague definition through the *escaping tendencies*. Chemical thermodynamics sees "the real gas fugacity as an effective partial pressure, which replaces the mechanical partial pressure in an accurate computation of the chemical equilibrium constant", or as "an analog of pressure that allows to calculate the change in the Gibbs energy as a function of pressure". These definitions are also vague.

For equation (1) the initial condition is: $D_{m\,1} = 2\,D_{P\,1} - D_1$ (Sedunov 2012). And the digital solution (Sedunov 2010) for the equation (1) is:

$$D_{m\,i} = D_{m\,(i-1)}\,(1 + \Delta D_P/(2D_{(i-1)}))/(1 - \Delta D_P/(2D_i)). \qquad (2)$$

Here ΔD_P is the step value along the column D_P. It is remarkable that the ΔD_P stays both in the numerator and the denominator. The solution (2) is valid also for the Fugacity digital computation. To compute the Fugacity the initial condition could be: $f_1 = 2P_1 - RTD_1$.

Results

The Canonical Coefficients Features

A large interest presents the correlation between canonical coefficients with different numbers. The Figure 4 shows the C_3 coefficient for Neon and its model expressed via C_2.
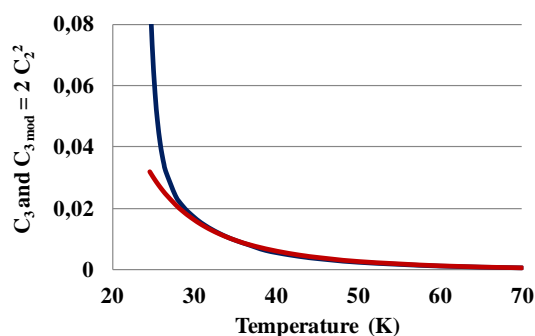

Figure 4. The third canonical PDT coefficient C_3 (blue line) and its model $2\,C_2^2$ (red line) in Neon.

The model expression was derived for the linear cluster isomer with two bonds. The C_3 coefficient corresponds to this model at T > 30 K. But near the triple point we see a large difference between C_3 and loosely bound

linear cluster isomer model. Therefore, at T < 30 K the trimers in Neon have tightly bound isomers, which are responsible for the C_3 coefficient growth.

The Symmetry between Clusters in Vapor and Pores in Saturated Liquid in Normal Fluids

The symmetry between clusters in a saturated vapor phase and pores in a saturated liquid phase of normal fluids (NIST 2021) is demonstrated by the Figure 5. At this figure together with saturated vapor and liquid densities for Nitrogen their sum and the middle line, sum/2, are shown.
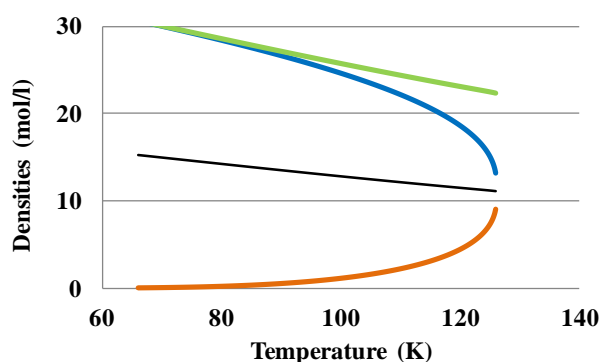

Figure 5. Saturated vapor density D_v (red line), saturated liquid density D_l (blue line) in Nitrogen, the sum $D_v + D_l$ (green line), the middle density (black line).

A similar feature was noticed for: H_2, H_2S, CO, CO_2, F_2, SO_2, and many other fluids (NIST 2021), which may be named as normal. The Figure 5 shows that the saturated densities sum in a normal fluid is a straight line and the middle straight line aims at the critical point. The tangents of slope for D_{sum} (T) for these and some other fluids are shown at the Table 1. There is also shown the linear part share LP as the linear T range to the total ($T_{cr} - T_{tr}$) range ratio. In normal fluids LP = 1 and in polar fluids LP < 1.

Table 1. The tangents of slope K_{sum} for the D_{sum} (T) straight line part and the linear part share LP.

Fluid	$K_{sum} = dD_{sum}/dT$	$LP = T_{lin}/(T_{cr} - T_{tr})$
H_2	-0,0115	1
CO	-0,0155	1
H_2S	-0,0211	1
SO_2	-0,0217	1
F_2	-0,0265	1
CO_2	-0,0664	1
NH_3	-0,0543	0,99
Ne	-0,0222	0,93
Methanol	-0,0317	0,74

So, in normal fluids we see a mirror symmetry of saturated densities with the middle line as a mirror. It means:

the cluster density in the vapor is equal to the pores density in a liquid at the same temperature in a normal fluid. In polar fluids, as Water and Heavy water, there is no linear part of the D_{sum} graph, Figure 6. The difference between the D_{sum} in the H_2O and D_2O is small. But in the Methanol a long linear part is present, Table 1.
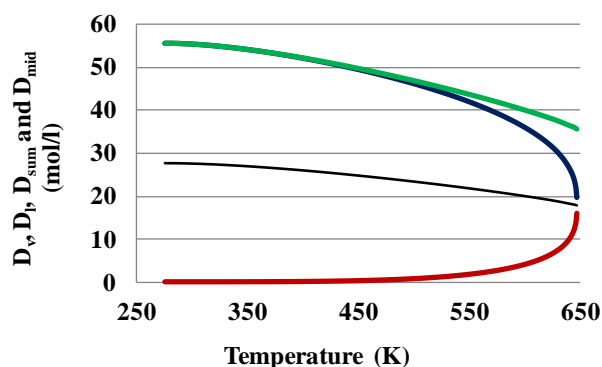
Figure 6. High curvature of the D_{sum} (T) in Water: D_{sum} (green line).

No polar fluid, Neon, (NIST 2021) has a small curvature of the D_{sum} (T) at near critical T, Figure 7. It may be caused by the giant bond energy clusters dissociation.
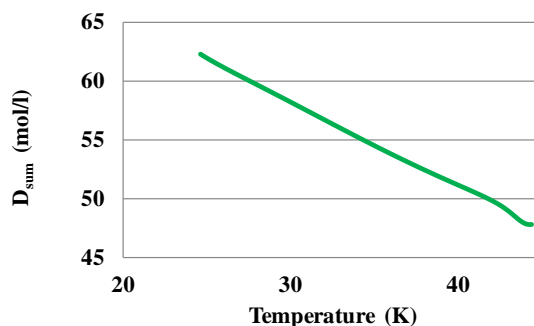
Figure 7. The curvature of the D_{sum} (T) in Neon.

These interesting features wait for their explanation. It is a challenging task for students!

Discussion

In the Results section we have shown only unpublished before results. Their originality tells that the cluster physics can bring a lot of new results. The developed methods of investigations in the cluster physics create a solid basis for this new chapter in thermodynamics. It should motivate the researchers, teachers and students for a deep study and own research of clusters. The canonical expansion creates rich opportunities for new discoveries!

Conclusion

The canonical cluster expansion avoids the virial expansion errors, for this reason it leads to a correct cluster physics and has a large potential for new discoveries.

The pure gases chapter presents not only its own content, but also shows how to solve problems of other chapters in thermodynamics education.

Recommendations

In the real gases study, we should start from pure gases and their remarkable features and to study the cluster physics, basing on precise thermophysical data analysis.

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