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Review: *Discovering the Cluster World. Clusters' Hidden Parameters Extraction from Thermophysical Data* and *The Wonders of Molecular Interactions. The Experimentally Based Molecular Interaction Features*

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Abstract

Nowadays, physical chemistry is intensely discussing studies of macroscopic, atomic, subatomic, and particulate phenomena in chemical systems that are closely connected to clusters, clusters as host molecules for other guest molecules. The clusters as host molecules for other guest molecules could be described as adducts. Intermolecular forces, reaction kinetics and rates of reaction, surface chemistry and electrochemistry of membranes, the electrical conductivity of materials and the identity of ions, electrochemical cells, and many other phenomena depend on the presence and state of cluster molecules and adducts. This review discusses two popular books that give readers an introduction to the theory behind the subject. Together with this theory, several practical approaches for applications described in the above books are discussed and explained.

Keywords

Clusters, Chromatography, Mass Spectrometry, Nature, Books, Supercritical Fluids, Extraction

1. Introduction

The book *Discovering the Cluster World. Clusters' Hidden Parameters Extraction from Thermophysical Data* describes the properties of clusters and molecular interactions in real gases and supercritical fluids (SFs). Real gases and SFs are now widely used in technological processes and analytical methods such as SF chromatogra-

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phy (SFC) and SF extraction (SFE) [1]-[8]. SFs partly consist of clusters. This requires a better understanding of cluster physics in dense gases and SFs. The clusters are molecular complexes bound together by weak intermolecular forces [9]. They are less stable than chemical compounds, but nevertheless very influential. The clusters are responsible for pressure-dependent parts of many thermophysical functions. They influence the properties of technological gases, the high density of which precludes utilization of a simplified ideal gas model. The thermal movement perturbs the clusters' energy levels and hides the clusters' parameters from direct experimental study. Spectroscopy, which is extremely productive in molecular physics, does not work for equilibrium clusters. The existing theories of fluids do not describe in full detail clusters' properties in gases [10].

2. The Book *Discovering the Cluster World*

The new book *Discovering the Cluster World*. *Clusters' Hidden Parameters Extraction from Thermophysical Data* [11] describes new methods and the results of equilibrium clusters (by equilibrium clusters, the author of the book, Prof. B. Sedunov means "the clusters, which are in thermal and chemical equilibrium with surrounding medium, unlike the clusters created in molecular beams"). In pure gases, exploration has been based on precise experimental data from modern electronic databases, such as the USA's National Institute of Standards (NIST) and Technology Thermophysical Properties of Fluid Systems [12] databases. Computerized analysis of these data has proven informative for single-component gases. The developed methods are based on a quite new approach to clusters and permits discovery of the main characteristics and bond parameters of clusters. As described by Sedunov, the analysis uncovers the previously unknown class of one-dimensional (1-D) linear chain clusters [13], which dominate in a wide range of temperatures and densities over 2-D and 3-D clusters. The knowledge of mechanisms of these clusters' formation has led to the equations of state for the chain clusters' domination zone. The characteristics of chain clusters that are found can be extrapolated to high density levels, up to the critical point density. It permits exclusion of the contribution of chain clusters from experimental thermophysical properties and concentrates attention on the 3-D clusters, which determine the behavior of gases in the near-critical and supercritical regions. Hence, the analysis brings many surprising and educational results. These have been described as different phenomena, connected with clusters, such as formation of dust clouds in space; the transformations of water clusters in the atmosphere in addition to the early published work [14] [15] and water clusters formation in laboratories; the cooling effect of water clusters and the clusters' role in the extraction of aromatic substances from flowers and vegetation; the role of clusters in living cells; clusters as nucleation centers; and transformation of invisible clusters into visible snowflakes, droplets [16], and particles of dust [17].

To extract the molecular interaction and clusters' properties from precise thermophysical data, Sedunov has developed the hybrid-intellect method supported by the hybrid-researcher-computer interactive system. This system permits a researcher to select optimal data processing algorithms and to estimate the results of the computation in a visual form. A quick feedback between formulation of new algorithms and visualization of results helps to arrive, after several iterations, at a physically correct final version of an algorithm, which reveals new features of molecular interactions in clusters. The author bases his method on the series expansion of thermophysical values by the monomer fraction density, introduced by the author in the family of thermophysical variables [18]. The book describes traps met during research on cluster characteristics, based on the results of series expansions, and ways to solve the problems that arise. (*In a personal communication, the author explains his definition of* "*traps met*" *as*: "*In my investigations I have met a number of traps, such as wrong utilization of virial expansions by total density or total pressure*. *To avoid this trap, I use as an argument for series expansions of thermophysical values the monomer fraction density*. *This approach respects the mass action law*!") As the most informative thermophysical value, the author utilizes the potential energy density of a real gas [19]. This choice corresponds to the mass action law [20] [21]. Sedunov estimates the computational errors and shows how they can be reduced by proper selection of the working dataset to be analyzed. It has been shown that the temperature dependence for clusters' bond energies in many gases demonstrates the soft structural transitions between different isomers of clusters. For the region of chain clusters' domination, a system of equations of state has been derived. The author describes the geometric progression law for parameters of chain clusters with a growing number of particles [22]. This law permits estimation of the bond parameters of chain clusters without extra computations and extrapolation of the chain clusters' contributions up to the critical density. This extrapolation is the key factor in the investigation of large 3-D clusters, which is very important for the improvement of

SF technologies and analytical methods [23]. These ideas and methods had been further developed in the book *The Wonders of Molecular Interactions. The Experimentally Based Molecular Interaction Features* [24].

3. The Book *The Wonders of Molecular Interactions*

This book explains the complexity of extracting hidden parameters from experimental data, which is related to the class of ill-defined inverse mathematical problems [25]. The inverse problem decision has large errors at smallest deviations of initial data from regular dependencies. However, the data regularization in the electronic NIST database [12] permits solving the inverse problem of molecular interaction characteristics estimation with an acceptable precision. The author shows how to account for the virtual clusters appearing in the computational process. There are numerous illustrations in the book of unusual features in the thermophysical properties of many gases requiring an individual approach to different gases. The book demonstrates the importance of taking into account the elastic collisions of monomers in the computation of the pair bond parameters in dimers. To estimate the contribution of the monomers' collisions, a theory of the pair-interaction potential energy was built in addition to Mayers' theory of pressure-density relations in dimers [26]. The analysis of experimental data and the developed theory demonstrate the contribution of monomers' collisions to the potential energy of a gas, growing with the growth of the repulsion potential elasticity; this factor may lead to the irreversibility of processes in real gases.

The author presents the high bond energies of clusters in several gases, which may result from some sort of weak chemical bonding. A fruitful utilization of the constant volume heat capacity has been demonstrated for estimations of pair bond energies in dimers and for investigations of the gas-to-liquid transitions in SFs. Explanations have been given for linear chain cluster formation via instantaneously induced dipoles in a pair of molecules, which attract new molecules toward their opposite sides by inducing instantaneous dipoles at a distance. The substitution of clusters in the gas-like SFs on the bubbles in liquid-like structures above the critical density has been described. The investigation of this mechanism is very important for further improvement of the SF technologies.

4. Conclusions

In recent decades, the use of SFs in the extraction of compounds from plants and raw materials has received more and more practical interest, especially in the coffee-producing industry [27]-[29] and for extracting bioactive substances [30]. The processing of polymers [31], regeneration and synthesis of catalysts with CO_2 in a supercritical state [32] have become multimillion dollar businesses and the processing of waste from the chemical [33] and atomic energy industries [34] is an important environmental issue. The importance of the use of SFs in SFC, especially in isomer separation, is difficult to overestimate [1]-[8] [35].

The practical use of SFs needed the development of a theoretical basis, which in part is given in these books [11] [24].

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