ANALYSIS OF THE VAN DER WAALS CUBIC EQUATION OF STATE: FROM CLASSICAL THERMODYNAMICS TO STATISTICS

ANÁLISIS DE LA ECUACIÓN CÚBICA DE ESTADO DE VAN DER WAALS: DESDE LA TERMODINÁMICA CLÁSICA HASTA LA ESTADÍSTICA

Sebastián Gómez Páez*

https://orcid.org/0000-0002-3798-2728

UNIVERSIDAD NACIONAL DE EDUCACIÓN A DISTANCIA, ESPAÑA

Resumen

Hoy en día, el equilibrio entre vapor y líquido se estudia y realiza, normalmente, utilizando programas de simulación que permiten a los ingenieros desarrollar diseños, avances y nuevas investigaciones, evadiendo el emocionante análisis de la termodinámica molecular desde sus fundamentos, ya que paquetes computacionales como Aspen® o CHEMCAD® incluyen la mayoría de las ecuaciones de estado disponibles y adecuadas, según el sistema bajo estudio. Sin embargo, el desarrollo ulterior de nuevas y mejores correlaciones para predecir, y, posteriormente, modelar el equilibrio entre vapor y líquido puede detenerse por la novedosa ingeniería química computacional; por esta razón, en este documento se formula una demostración procedimental de cómo la ecuación de Van der Waals, la más famosa y fructífera ecuación de estado, es discernida desde el punto de vista de la termodinámica clásica y la estadística, e incluye una detallada ilustración fenomenológica y matemática acompañada de un caso de estudio.

Palabras clave: equilibrio entre vapor y líquido, termodinámica estadística, ecuación cúbica de estado, Van der Waals, colectivo, función de partición

Abstract

Nowadays, vapor-liquid equilibrium in chemical engineering is commonly studied and tested by using simulation software that allows engineers to build up designs, advances and new researches avoiding the thrilling molecular thermodynamic analysis from its foundations, because computing packages such as Aspen® or CHEMCAD® have already included the most of the available equations of state (EoS), which suit depending on the studied system. Nevertheless, the major development of new and better correlations to predict and subsequently model the vapor-liquid equilibrium could be halted by the recent computational chemical engineering, for that reason, in this paper,

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* Ingeniero Químico, Fundación Universidad de América, Bogotá D. C., Colombia; estudiante de maestría en Ciencias y Tecnología química, UNED, España. ✉ sgomez935@alumno.uned.es

a procedural demonstration of how the Van der Waals (VdW) equation —the most famous and resulting EoS for years— is stated and developed from the point of view of both classic and statistical thermodynamics. A detailed phenomenological and mathematical description is showed, including a numerical case of study.

Keywords: vapor-liquid equilibria, statistical thermodynamics, cubic equation of state, Van der Waals, ensemble, partition function.

INTRODUCCIÓN

The foundations of vapor-liquid equilibrium (VLE) have been considered as a wide range of separation processes including conventional and non-conventional distillation, absorption, etc., because the phase to split involves complex molecular phenomena that must be modeled in order to achieve a reliable simulation that is subsequently needed to design and scale up a separation process (Chen *et al.*, 2018; Kraemer, *et al.*, 2011; Leon, Palacios-Bereche & Nebra, 2016; Niesbach *et. al.*, 2015; Toikka, Naumkin & Penkova, 2015); thus, the necessity of mathematical models to represent the VLE has been stepping up due to the complexity of some systems such as those that present stood out nonidealities, electrolytic properties or associations (Kontogeorgis & Folas, 2009). As a result of that necessity, several models have been proposed, developed and applied in order to provide the best agreement with the experimental results in VLE engineering endeavours. Nevertheless, the advancement in powerful EoSs such as CPA, PC-SAFT or even classic EoSs with modifications that include energy-based mixing rules (Poling, Prausnitz & O'Connell, 2001), have could not been made in absence of the earlier development of the VdWEoS, because it was the starting point in the design of high-performance vapor-liquid-based separation processes. Among the different functions the EoSs offer in chemical engineering the computation of both liquid and vapor densities, vapor pressure, critical points, VLE simulated data and deviations of thermodynamic properties such as enthalpy and entropy are available by bringing the proper numerical handling to bear (Walas, 2013).

Classic thermodynamics, which (a) allows its completely characterization through the equilibrium supposition based on the internal energy (U), volume (V) and number of particles (N) as its describing properties, (b) introduces the entropy (S), as a function depending on U, V and N, that is maximum in isolated systems, (c) and defines S as continuous, differentiable and increasing with regard to U and as an additive property over all the constituent subsystems and (d) states null S at 0 K (Callen, 1998). It provides a general point of view in which a widespread analysis of the system is given by considering the atoms as an only one macroscopic and continuous assembly. Unlike classic thermodynamics, statistical thermodynamics has its basics via the following postulates: (a) a system's *ensemble* is suitable to represent the general behavior of the considered system and (b) thought for an isolated thermodynamic system. The members composing the *ensemble* are distributed with the same probability over the possible quantum states of the system given by U, V and N (Laurendeau, 2005). The concept of *ensemble* has been considered along the statistical thermodynamics principles since it is the easiest way to study large systems pointing to the order of the Avogadro number

for robust analysis; thus, it is defined as a very both large and theoretical assembly of subsystems that replicate the macroscopic thermodynamic properties of the main system. It could be classified as microcanonical, canonical, grand-canonical and isothermal-isobaric ensemble, depending on the specified U, V and N conditions (McQuarrie, 1977). Since the ensemble is applicable for a large variety of thermodynamic systems, one might remember that U, V and N could be specified by knowing the pressure (p) and the temperature (T) as well. In this manner, a function such that one can both relate and include those variables, establishing the partition function which is defined later.

This paper describes thorough an introduction, illustration, review, step-by-step demonstration and an application how Van der Waals EoS's for pure substances are derived from the statistical thermodynamic point of view, because it has been considered the most famous and fruitful one, due to its simplicity and easy use even when it does not provide the best results in the simulation of vapor-liquid-based separation processes. It begins analyzing the classic sight that considers the original model, it continues with the study of both the molecular and phenomenological approaches of the statistical field pondering the numerical strategies suitable to overcome every resulting difficulty during its introduction. Finally, a discussion about the importance of these endeavours is carried out under the sight of the modern challenges in chemical engineering recalling the need for development of new models that exemplify even more the experimental results.

VAN DER WAALS' EoS: EARLY REVIEW

Many authors have been analyzing, modifying and extending the VdWEoS due to its simplicity and slightly good harmony with most of the systems considered and studied. That is why is classified as the most famous and fruitful EoS. Proposed in 1873, it was originally mentioned as "on the continuity of the gas and liquid states" (Walas, 2013) because the ideal gas equation is not suitable for the requirements stated by the science and technology due to its molecular considerations and limitations. In such way, it is mathematically defined in eqn (1):

$$p = \frac{RT}{\bar{v} - b} - \frac{a}{\bar{v}^2}$$ (1)

Unlike the ideal gas equation, it introduces the parameters a and b, which are referred to the attraction and repulsion parameters respectively, considering that those facts are neglected in the ideal gas equation. The mathematical expressions to obtain a and b are illustrated elsewhere (Atkins & De Paula, 2017; Greiner, Neise & Stöcker, 1995; Prausnitz, Lichtenthaler & de Azevedo, 1998; Seader & Henley, 2011) and they might be further used to model the VLE for closely-ideal mixtures (Prausnitz *et al.*, 1998). A remarkable matter of fact is exposed when the VdWEoS is derived as follows:

$$\frac{\partial P}{\partial \bar{v}}\bigg|_T = \frac{\partial^2 P}{\partial \bar{v}^2}\bigg|_T = 0 \tag{2}$$

Because of the law of the corresponding states that leads to the quantification of the reduced properties, so the parameters a and b are called off and the *reduced equation state* could be stablished as:

$$p_r = \frac{8T_r}{3\bar{v}_r - 1} - \frac{3}{\bar{v}_r^2} \tag{3}$$

Nowadays, VdW equation is obsolete for industrial applications; nevertheless, it is considered the starting point to develop new and more precise EoSs because those have shown suitability for most of the industrial applications (Kontogeorgis & Folas, 2009).

VAN DER WAALS' EoS: STATISTICAL THERMODYNAMICS APPROACH

Now, the concept of N, V, T-dependent ensemble is treated in order to illustrate how to come to the eqn (1) starting from the canonical partition function, because the VdW's EoS is proposed considering the canonical ensemble (Sesé & Criado, 1990); thus, its quantum version is stated based on:

$$Z(N, V, T) = \sum_i \exp(-\beta E_i) \tag{4}$$

Whereas β is the canonical parameter and E_i represents the energy at the ith quantum state. This one is rarely used because the classic version is more suitable based on its clearer mathematical step:

$$Z(N, V, T) = \frac{1}{h^{3N}N!} \int \cdots \int exp[-\beta H(\boldsymbol{q}^N, \boldsymbol{p}^N)] \, d\boldsymbol{q}^N d\boldsymbol{p}^N \tag{5}$$

This equation leads to think that the partition function considers both the $\boldsymbol{q}^N$ space and the $\boldsymbol{p}^N$ momentum contribution, taking into account that the Hamiltonian H is evaluated for each N molecule, therefore eqn (5) is set as an assembly of $9N$ multiple integrals when all the coordinates are under study. Furthermore, the energy-based

Hamiltonian operator involves both the kinetic (K) and potential (U) effects. It means that both the motion and interaction among molecules contributions are contemplated. Without detailing, eqn (5) could be limited by splitting it into the translational part, and the configurational integral that is no more than the $\boldsymbol{q}^N$ could be associated integral term in eqn (5):

$$Z(N,V,T) = \frac{1}{h^{3N}N!}Z_{translational}\,Q(N,V,T) \tag{6}$$

$$Z_{translational} = \int \cdots \int exp[-\beta K(\boldsymbol{p}^N)]\,d\boldsymbol{p}^N \tag{7}$$

$$Q(N,V,T) = \frac{1}{V^N}\int \cdots \int exp[-\beta U(\boldsymbol{q}^N)]\,d\boldsymbol{q}^N \tag{8}$$

The central focus now is the configurational integral because it has the key to transcend from the non-interacting contributions to the interacting ones, via the perturbation theory (McQuarrie, 1977); thus, the potential energy in eqn (8) is defined such as it is divided into a reference part, $U^{(0)}$, and a perturbation, $U^{(1)}$, based on:

$$U(\boldsymbol{q}^N) = U^{(0)}(\boldsymbol{q}^N) + U^{(1)}(\boldsymbol{q}^N) \tag{9}$$

Hence, the previously defined configurational integral is now:

$$Q(N,V,T) = Q^{(0)}\langle exp[-\beta U^{(1)}]\rangle_0 \tag{10}$$

Eqn (10) has its agreement based on the hard spheres (h,s) model, because otherwise, it would not be possible to open eqn (11) as:

$$U(\boldsymbol{q}^N) = U^{(0)}_{h,s} + U^{(1)} = \sum_{1\leq i<j\leq N}\left[u^{(0)}(r_{ij}) + u^{(1)}(r_{ij})\right] \tag{11}$$

Whereas r_{ij} is defined as the distance between the ith and the jth particle, and $u^{(1)}$ as the paired additive interaction energy that is constrained to be negative in order to

consider the attractive interactions, in such a way the canonical average is convenient to be reframed as follows:

$$\langle exp[-\beta U^{(1)}]\rangle_0 \approx 1 - \beta \langle U^{(1)}\rangle_0 \approx exp[\langle -\beta U^{(1)}\rangle_0] \tag{12}$$

The potential energy is computed at the perturbation considering the correlation function *g*:

$$\langle U^{(1)}\rangle_0 = 2\pi\rho^2 V \int_0^\infty u^{(1)}(r)g^{(0)}(r)r^2 dr \tag{13}$$

Which is effectively approximated via the hard spheres foundation (McQuarrie, 1977) when the density tends to be null, hence:

$$\langle U^{(1)}\rangle_0 = 2\pi\rho^2 V \int_0^\infty u^{(1)}(r)r^2 dr < 0 \tag{14}$$

And subsequently:

$$\langle U^{(1)}\rangle_0 = -aN\rho \quad \therefore \quad a > 0 \tag{15}$$

$$a = 2\pi \int_0^\infty u^{(1)}(r)r^2 dr \tag{16}$$

Up to this point, the *a* term has been statistically defined and it leads to:

$$Q(N,V,T) = Q^{(0)}exp[\beta aN\rho] \tag{17}$$

In which $Q^{(0)}$ is known by recalling the statistical-based average pressure (Sesé & Criado, 1990):

$$\langle p \rangle = k_B T \left[\frac{\partial \ln(QV^N)}{\partial V} \right]_{N,T} \tag{18}$$

Since the previous demonstration of a and the partial differentiation of $ln(QV^N)$ respect to V at constant both N and T, the average pressure could be stated as:

$$\langle p \rangle = p^{(0)} - a\rho^2 \tag{19}$$

Whereas $p^{(0)}$ is the pressure at the reference state and it results from the ideal gas equation because since its partition function equation is matched to the unity, and the particles are rigid (impenetrable), there is an effective volume for each particle that limits the intermolecular interactions, and it is assumed to be equal to the half of a single molecule's total volume considering its σ radius; thus:

$$V^{eff} = \frac{1}{2}V = \frac{2}{3}\pi\sigma^3 \tag{20}$$

Considering the effective volume, it is necessary to exclude the reachable volume during the interactions; thus, eqn (21) results in:

$$V^{reachable} = V - \frac{2}{3}\pi\sigma^3 = V - NV^{eff} \tag{21}$$

Since the effective volume is specified, it is convenient to set it as b rather than V^{eff} in order to state that the reachable volume accounts the subtracted N effective volumes b for each molecule. In this way, the configurational integral for the reference state is now projected:

$$Q^{(0)} = \frac{V - Nb}{V} \qquad \therefore \qquad b = \frac{2}{3}\pi\sigma^3 \tag{22}$$

Therefore, the differentiation for the average pressure turns out as follows:

$$\langle p \rangle = \frac{Nk_BT}{V - Nb} - a\rho^2 \tag{22}$$

Which is equivalent to the eqn (1) but in terms of the density and considering the constants a and b with respect to the intermolecular potential functions. In addition further applications of the VdWEoS allow both the quantification of the critical point and condensation -due to its simplicity- and the enhancement of some procedures such as better forms for the correlation function, the approach to more realistic unperturbed systems, better expressions for the configurational integral and higher terms in β, in order to roll out the VLE's analysis.

VAN DER WAALS' EoS: CORRELATIONAL ACCURACY

In order to test the accuracy of the VdWEoS, a case of study developed by Ibrahim *et. al.* (2014) was considered to reproduce the figure 1, in which the density is computed at several pressures, 400 °C and two carbon dioxide's compositions. Eqn (1) was used to compute the pressure in order to avoid the calculation of multiple roots for the volume or density. Quadratic mixing rules for a and b factors were applied because of their more precise concurrence as seen in eqns (23) and (24). The results are shown in figure 1, which was made using Matlab®.
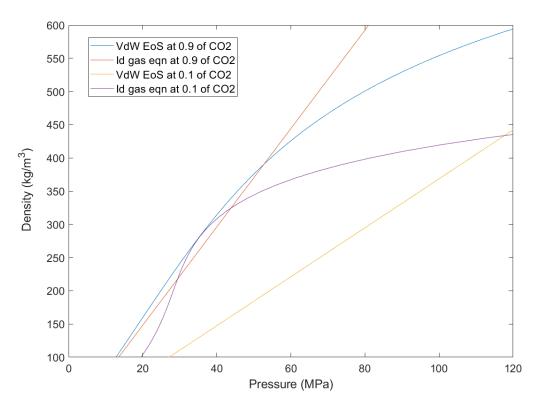
$$a_{mix} = \sum_{i=1}^{c}\sum_{j=1}^{c} x_{ij}x_{ji}a_{ij} \tag{23}$$

$$b_{mix} = \sum_{i=1}^{c}\sum_{j=1}^{c} x_{ij}x_{ji}b_{ij} \tag{24}$$

Ibrahim, *et al.,* (2014) developed the density profile rather than the pressure one made in this paper. Even so, the results have a common tendency, notwithstanding the difference is higher than the 5 % for the calculations depicted with the VdWEoS; thus, this EoS allows researchers to obtain a first approximation that could be extended further towards a more rigorous model, a one hardly convergent when no previous system information is available. On the other hand, at low carbon dioxide's compositions, it means high water's compositions, a polar behavior is showed up; thus, the computed pressure differs in more than the 30 % when the VdWEoS and the ideal gas are matched up because they are unworthy to predict the gas behavior been unsuitable for polar interactions, then associations are present (Yokoyama, Arai & Saito, 1984; Kontogeorgis & Economou, 2010).

Figure1.

Pressure profile as a function of the density.

Note. Figure shows that at high carbon dioxide's composition, the computed pressure, by using both the VdWEoS and the ideal gas equation, has a similar behavior at low densities because above 400 kg/m^3 it differs significantly.

CONCLUSIONES

A phenomenological and mathematical discussion with demonstration of the VdWEoS was presented in this paper in order to enhance its importance as the EoS's precursor during the earlier years. Starting from the classic point of view throughout the statistical approach of thermodynamics -which includes the ensemble's conception, the intermolecular interactions, the spatial arrangement and the behavior of the studied molecules- the EoS's foundations provide a strong tool in chemical engineering to propose design and simulate separation processes based on the VLE, since EoSs are useful, accurate and reliable when suitable previous knowledge —theoretical and experimental— is applied in order to enhance its application.

Further researches will lead to the proposal of new EoSs, which will provide even more accurate results with less computing time, operational cost and intellectual effort. Nevertheless, the prediction and modeling of noncommon molecular interactions such as hydrogen bonds, associations, dimerizations and of the electrical properties result in effort-consuming procedures because longer expressions are needed to correctly

investigate those interactions. In addition, the statistical-thermodynamic-based ensemble's mathematical modeling is even longer and time-consuming than the simple correlational proposal of cubic and high order EoSs. The solution of 9N integrals that have nonanalytical solution when strong and allow noncommon interactions is expected, even though their solution leads to highly accurate results but it should be carried out using the Monte Carlo simulation.

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