

SEMI-RATIONAL METHOD FOR THE CONSTRUCTION OF EQUATIONS OF STATE FOR LIQUIDS AND GASES

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Basic ideas of the perturbation theory of the liquid state were used to develop a general method for constructing the equation of state valid for liquids and gases. The compressibility factor was decomposed into three parts: the first part corresponds to reference hard spheres or hard convex bodies, the second one is an attractive term of the Van der Waals type and the third part is a small correction, the form of which may be determined from experimental isothermal pV data and for which several empirical expressions were proposed. Saturated vapour volumes of nonpolar substances were correlated successfully by the new method.

Still continuing numerous attempts¹ to find a proper equation of state which would describe the pVT and vapour-liquid equilibrium behaviour of fluids in both gaseous and liquid state and in wide temperature and pressure ranges only witness that this problem is far from being solved. Although it is well known² that an analytical $p = p(V, T)$ dependence is in direct contrast with experiment in the very vicinity of the critical point, it would be wonderful to have such a dependence working within experimental accuracy for data not too removed from this point and especially along the vapour-liquid coexistence line. It would represent a possibility of extending this relation to mixtures and, with proper combination rules, of calculating their equilibrium properties in both gaseous and liquid state which are necessary for engineering applications.

In developing equations of states, different reference states had been used in the past. The BWR equation is the prominent representative of the reference state taken at the infinite dilution ($q \rightarrow 0$), *i.e.* of the virial expansion approach. This results in a necessity of using additional terms if properties of liquids are to be calculated. It does not follow from any theory what forms should such additional terms assume and, consequently, good equations of state of this type are rather a matter of serendipity. Several more³ or less^{4,5} successful attempts to extend the BWR equation and to generalize its constants should be cited here as examples.

Another approach is to use the liquid state as the reference and to find correction terms which must be added subsequently. It is the basis of the perturbation theory⁶ which postulates that repulsive forces are predominantly responsible for the structure of fluids at higher densities and that attractive forces can be treated as a small perturbation to effectively infinite repulsive forces at smaller intermolecular distances. It has been shown during the past decade⁶ that the perturbation theory is the only theory that can describe equilibrium thermodynamic properties of liquids

within experimental accuracy. According to this theory, the experimental compressibility factor z is composed of the compressibility factor corresponding to the reference state, z_{HB} , and of a correction term corresponding to the presence of attractive forces. It is known from both experiment and theory⁷ that this second term is proportional approximately to density. For the first term, z_{HB} , which may represent the contribution of hard spheres or hard convex bodies, almost exact expressions were found by solving the P - Y equation⁸ or by the scaled particle theory⁹. The only thing to be done is to find an empirical expression for the correction term remaining after subtracting these two terms from reliable experimental pVT data, that is for the third term, $s(\varphi)$, in the equation

$$z = z_{\text{HB}} - A/\varphi + f(\varphi)/\varphi, \quad (1)$$

where $\varphi = V/b$, b is proportional to a true volume of the molecule

$$z_{\text{HB}} = [\varphi^3 + \varphi^2(\gamma - 2) + \varphi(\gamma^2/3 - \gamma + 1)]/(\varphi - 1)^3, \quad (2)$$

$\gamma = 3$ for hard spheres and $\gamma > 3$ for hard convex bodies⁹, *i.e.* for molecules of nonspherical shape. More refined versions of the perturbation theory^{10,11} treat b as a both temperature- and density-dependent constant. We disregard this density dependence in our paper and consider only the temperature dependence of b .

The search for the correct form of the function $f(\varphi)$ in Eq. (1) should start with reliable pVT data on a substance for which a relation $\gamma = 3$ may be assumed. Argon fulfills undoubtedly these criteria; it is of spherical shape and good pVT data measured by Michels and coworkers¹² are available. We could now plot the values of $(z_{\text{HB}} - z)/\varphi$ against φ if we knew the value of b . This value can be assessed by using again the perturbation theory, namely from the value of the size parameter σ in the L-J 12 : 6 potential¹¹ and from the value of a parameter with which the constant σ is to be multiplied to obtain diameters of reference hard spheres¹⁰. It leaves us with an approximate value for b of argon near the critical point, $b_c = 11.3 \text{ cm}^3/\text{mol}$, which should be correct within $\pm 10\%$. It leads to the value of φ at the critical point $\varphi_c = 6.65$.

The plot of $(z_{\text{HB}} - z)/\varphi$ against φ with the experimental pVT data on argon at the reduced temperature $T_r \equiv T/T_c = 1.015$ is on Fig. 1 for three values of φ_c : 6.0, 6.673 and 7.0. It is seen that especially curve 1 which corresponds to the most probable value of b_c , is of nice shape with a minimum near the critical density φ_c and almost symmetrical around this point. In view of the fact that the plot covers the pressure range up to 470 atm and that vertical oscillations of function $f(\varphi)$ occur in a narrow range, the task of finding an empirical formula for $f(\varphi)$ valid in the widest possible region of densities seems relatively easy. A similar behaviour of $f(\varphi)$ near the critical point has been observed for several other substances such as carbon dioxide, ammonia and even water, that is for the case of $\gamma > 3$, or $z_c < 0.291$.

We may now turn the problem, assume that the function $f(\varphi)$ has a maximum at $\varphi = \varphi_c$ on the critical isotherm (this corresponds to a minimum of the function $(z_{\text{HB}} - z)/\varphi$) and try to find consequences of this assumption on the solution of the following conditions describing the critical point

$$z_c = z(\varphi_c), \quad p'(\varphi_c) = 0, \quad p''(\varphi_c) = 0. \quad (3)$$

The requirements on the form of the function $f(\varphi)$ may be expressed as

$$f'(\varphi_c) = 0, \quad f''(\varphi_c) < 0. \quad (4), (5)$$

Substituting from Eq. (1) into Eqs (3), performing some of the differentiations and taking into account condition (4) we have

$$z_c/\varphi_c = z_{\text{HB}}/\varphi_c - A/\varphi_c^2 + f(\varphi_c)/\varphi_c^2, \quad (6)$$

$$0 = \varphi_c/2(z_{\text{HB}}/\varphi)'_c + A/\varphi_c^2 - f(\varphi_c)/\varphi_c^2, \quad (7)$$

$$0 = \varphi_c^2/6(z_{\text{HB}}/\varphi)''_c - A/\varphi_c^2 + f(\varphi_c)/\varphi_c^2 - f''(\varphi_c)/6. \quad (8)$$

By adding Eqs (6) and (7) and for $\gamma = 3$ it is possible to obtain the following relation

$$\varphi_c^4 - 4\varphi_c^3 - 4\varphi_c^2 - 2\varphi_c - 2z_c(\varphi_c - 1)^4 = 0 \quad (9)$$

which on solution yields $\varphi_c = 6.6730$ for the critical compressibility factor of argon $z_c = 0.291$. Condition (4) thus leads directly to a value of φ_c , which is in good agreement with the expected value of 6.65 and this result is independent of the particular shape of $f(\varphi)$. The curve corresponding to $\varphi_c = 6.673$ is on Fig. 1 and it is denoted by 1. One of possibilities which should be followed further is to minimize differences between $(z_{\text{HB}} - z)/\varrho$ of argon for $\varphi_c = 6.673$ and an empirical function $g(\varrho) \equiv f(\varphi)$.

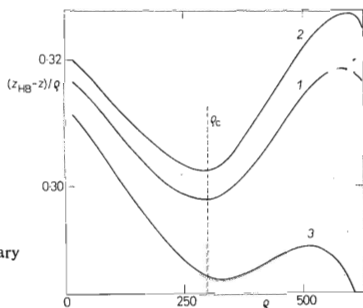


FIG. 1

Dependence of $(z_{\text{HB}} - z)/\varrho$ on ϱ (arbitrary units) for Argon at $T_r = 1.015$

1 $\varphi_c = 6.673$, 2 $\varphi_c = 6.0$, 3 $\varphi_c = 7.0$.

This procedure could yield constants of the empirical function in the vicinity of the critical point and simultaneously decide among several functions $f(\varphi)$.

If we retain a general γ in Eqs (6)–(8), we can obtain by eliminating the difference $A-f(\varphi_c)$ the following two equations

$$\gamma^2(\varphi_c + 2) + 6\gamma(\varphi_c - 1) - 3\varphi_c^3 + 12\varphi_c^2 - 15\varphi_c + 6 + 6z_c(\varphi_c - 1)^4/\varphi_c = 0, \quad (10)$$

$$\gamma^2(\varphi_c + 3) + 6\gamma(\varphi_c - 1) - \varphi_c^3 + 5\varphi_c^2 - 7\varphi_c + 3 + [(\varphi_c - 1)^5/\varphi_c] \cdot [f''(\varphi_c)] = 0. \quad (11)$$

These two quadratic equations can be easily solved for γ (positive discriminants in both cases) to yield a nonlinear equation for φ_c . This nonlinear equation would contain z_c and $f''(\varphi_c)$ as parameters. The value of z_c is an experimental quantity with which nothing can be further done. Some possibilities are open only for the second derivative of $f(\varphi)$ in the critical point, $f''(\varphi_c)$. If we assume that

$$f''(\varphi_c) = C\varphi_c^n, \quad (12)$$

where n is an integer, we can estimate the influence of n on the values of φ_c and γ resulting from the solution of Eqs (10) and (11) at different values of $z_c < 0.291$. It can be shown by a numerical solution of these two equations that if the value of C in Eq. (12) is taken from argon then $\gamma > 3$ only if $n \geq 0$; for $n < 0$, it always holds $\gamma < 3$ which lacks any reasonable physical interpretation. Thus, for example, the value of n equal to zero at $z_c = 0.23$ corresponds to $\gamma \sim 8.3$ and $\varphi_c \sim 10.8$. Little is known of the exact magnitude of the constant γ except that it must hold $\gamma > 3$. As far as the value of φ_c is concerned we may resort to values of constants σ in the L-J 12 : 6 potential as tabulated by Hirschfelder and coworkers¹³ or Reid and Sherwood¹⁴. We know that the ratio $V_c/N\sigma^3$ should be approximately proportional to φ_c and so we can compare this ratio for different substances with that for argon. Unfortunately we arrive at rather controversial results. According to the tabulated values of σ , the values of φ_c depart from that for argon on opposite sides for polar and nonpolar substances, so that it holds

$$(\varphi_c)_{\text{nonpolar}} < (\varphi_c)_{\text{Ar}} < (\varphi_c)_{\text{polar}}. \quad (13)$$

As the relation $\varphi_c < (\varphi_c)_{\text{Ar}}$ leads to $\gamma < 3$, it might suggest that the nonsphericity of molecules cannot be taken into account by the single constant γ and that constants in the function $f(\varphi)$ could be affected by the molecular shape, too. By solving Eq. (9) for $z_c < 0.291$ it may be shown that $z_c < 0.291$ leads to $\varphi_c < (\varphi_c)_{\text{Ar}}$ which is in

agreement with the left side of relation (13). On the other hand, the accuracy of the constants σ in comparison with differences between theoretical values of φ_c is so low that relation (13) cannot be considered as established definitely, at least on its left side. From the tabulated values of the constants σ of ammonia and water it appears that $\varphi_c \sim 10.0$ would be a good approximation and that $n = 0$ in Eq. (12) might yield reasonable results. The final decision of the problem whether the nonsphericity and polarity should be included in the function $f(\varphi)$, constant γ , or both of them, should be made on the basis of the direct comparison between experimental data and calculations using different acceptable forms of $f(\varphi)$.

We have also plotted experimental pVT data of different substances on the $(z_{\text{HB}} - z)/\rho$ vs ρ scale at subcritical and supercritical temperatures and with different values of b . The form of this dependence as depicted on Fig. 1 remains much the same at both $T < T_c$ and $T > T_c$. At $T < T_c$, there is a gap corresponding to the two-phase region, which becomes wider as the temperature decreases. This makes difficult any conclusive statements regarding the form of the function $f(\varphi)$. In order to preserve the symmetrical shape of $f(\varphi)$ at lower temperatures, it would be necessary to assume a slightly negative slope of db/dT which is in agreement with the perturbation theory. Physically, it means that the size of molecules decreases with increasing temperature. This trend continues to $T > T_c$. At supercritical temperatures, changes in the location

TABLE I

Mean^a/Maximum Absolute Percent Deviations in Calculated Saturated Vapour Volumes for Different Forms of Function $f(\varphi)$

Substance	T^b_r	Eq. (15)	Eq. (16)	Eq. (17)
Argon ¹⁷	0.58	1.5/4.6	0.7/1.0	0.9/1.3
Methane ¹⁸	0.52	1.5/8.5	1.1/3.6	1.3/3.8
Ethane ¹⁹	0.58	1.2/4.3	2.4/3.6	2.6/4.0
Propane ¹⁹	0.62	1.4/5.1	2.6/3.6	2.8/4.0
Butane ¹⁹	0.64	1.6/6.5	2.0/2.8	2.3/3.3
Carbon monoxide ¹⁸	0.51	2.9/5.4	2.6/6.3	2.8/6.6
Carbon dioxide ¹⁸	0.71	1.7/5.6	2.1/3.3	2.4/3.6
Cyclopropane ²⁰	0.74	1.9/6.1	2.7/3.7	3.1/4.1
Ammonia ¹⁸	0.49	4.1/7.3	6.8/18.0	7.4/18.0
Water ²¹	0.45	2.9/6.5	5.4/17.0	6.0/20.0

^a Mean deviation = $\Sigma 100 |V_{\text{calc}} - V_{\text{exp}}| / n_{\text{exp}} V_{\text{exp}}$. ^b Lower limit of the temperature range covered by the computations.

of the minimum on the plot have been observed. Irrespective of the choice of b , this minimum shifts slowly from ϱ_c to lower densities with increasing temperature. This holds for both spherical nonpolar ($\gamma = 3$) and nonspherical, possibly polar ($\gamma > 3$) molecules.

As far as the form of the temperature dependence of constants b , A , γ and constants in the function $f(\varphi)$ is concerned, only few theoretically founded suggestions exist. The molecular shape should not be affected much by temperature and consequently one would expect that constant γ could be temperature-independent. As absolute values of the empirical function $f(\varphi)$ are small compared with first two terms on the rhs of Eq. (1), one could also expect that the temperature dependence of $f(\varphi)$ would play a minor role in the determination of thermodynamic properties of fluids and that the corresponding constants could be also treated as temperature-independent. Of different constants in the function $f(\varphi)$, the temperature dependence would be perhaps most relevant for a constant corresponding to the location of the minimum of $f(\varphi)$ on the density axis. However, according to some preliminary calculations, the temperature dependence of both A and b cannot be neglected. The temperature dependence of A can be expressed by an arbitrary suitable empirical function. For the temperature dependence of b , the perturbation theory offers an expansion

$$b = b_1/T + b_2/T^2 + \dots \quad (14)$$

which follows from the formula developed by Barker and Henderson¹⁵ for the diameter of reference hard spheres. Thus, the recommended procedure for finding new equations of state for the description of behaviour of both gases and liquids consists of three steps:

1) to find a proper functional dependence for $f(\varphi)$ for spherical nonpolar molecules. This dependence should be found by an analysis of isothermal pV data at slightly supercritical temperatures, where it is plausible that $b = b_c$.

2) To decide whether nonsphericity and polarity can be included through the constant γ , function $f(\varphi)$, or both of them. This decision should also result from an analysis of slightly supercritical isothermal pV data.

3) To find a final form of the equation of state in which the temperature dependence of at least constants b and A would be included. This final form should result from a minimization procedure including extensive sets of reliable pVT data.

Calculations. We have made some preliminary calculations with three different forms of $f(\varphi)$ and for $\gamma = 3$:

$$f(\varphi) = -C(\varphi - \varphi_c)^2/\varphi^2, \quad (15)$$

$$f(\varphi) = C/[1 + 0.5(1 - \varphi_c/\varphi)^2], \quad (16)$$

and

$$f(\varphi) = C \sin(15/\varphi - 15/\varphi_c + \pi/2). \quad (17)$$

All these three functions have the necessary maximum at $q = \varphi_c$. The values of b , A and C were determined in the critical point by solving Eqs (6)–(8). The temperature dependence of C was neglected in further calculations and the test was performed on values of b , A and saturated vapour volumes V_{vap} calculated from the constant C and known experimental saturated vapour pressures p_s and saturated liquid volumes V_{liq} obtained by simultaneous solution of the following equations

$$p_s = p(V_{\text{liq}}), \quad p_s = p(V_{\text{vap}}), \quad p_s(V_{\text{vap}} - V_{\text{liq}}) = \int_{V_{\text{liq}}}^{V_{\text{vap}}} p \, dV. \quad (18)$$

The computations were made by the method due to Joffe and coworkers¹⁶ and they cover the temperature range from $T_r = 0.5$ – 0.6 to the critical point. Mean and maximum absolute percent deviations in calculated values of V_{vap} are given in Table I for ten substances with z_c in the range 0.23 – 0.29 . It is seen that best results for nonpolar substances are obtained with the help of Eqs (16) or (17) whereas saturated vapour volumes of highly polar and associated substances such as water or ammonia are reproduced best with Eq. (15). It is not obvious from Table I, but the maximum deviations are observed in the vicinity of the critical point. At lower temperatures, the agreement is within experimental error; this may be caused partially by lower pressures at which the vapour behaves more like the ideal gas. Another encouraging thing is that constants A and b depend only mildly on temperature; the total change in the whole temperature range amounts to 10 – 20% . The slope of the b vs T dependence is negative, as expected.

We hope that we will be able to improve these results by incorporating the constant γ into the equation of state and that the improved equation could be readily extended to mixtures.

LIST OF SYMBOLS

N	Avogadro's number	R	gas constant
p	pressure	$z = pV/RT$,	compressibility factor
V	molar volume	$q = N/V$,	density
T	absolute temperature		

Subscripts

c	critical point
r	reduced property

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