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Perturbation Method for Phase-Equilibrium Calculations[1]

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In phase equilibrium problems, the thermodynamic model used often contains a small parameter. For example, for cubic equations of state the interaction coefficients occurring in van der Waals-type mixing rules are often numerically small. The small parameter (ε) enters the model then via the formula

$$a = \sum_{i=1}^{n} \sum_{j=1}^{n} x_i x_j \sqrt{a_i a_j}(1 - \varepsilon\theta_{ij})$$

Other examples include mixtures with compounds whose characteristic parameters cover a narrow range, diluted solutions, small amounts of polydisperse material in a solvent, and so on. In this paper we develop a general scheme to obtain the solution of thermodynamic problems such as the prediction of phase equilibria, using an expansion in the small parameter ε. We also give a method to obtain a suitable zero-order ($\varepsilon = 0$) system. The perturbation scheme may be helpful in the solution of difficult problems or as a tool in a sensitivity analysis. As an example we apply it to multicomponent mixtures, described through a two-parameter equation of state with small interaction coefficients. We show that for that case, if the number of components is large, it leads to computational savings.

KEY WORDS: perturbation method; mixtures; thermodynamic properties; vapor–liquid equilibrium.

1. INTRODUCTION

In thermodynamics of phase equilibria one is concerned with problems such as the determination of a phase split at given pressure, temperature and mixture composition, bubble-point pressure at a given temperature

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and liquid composition, and so on. The principle behind such (equilibrium) calculations has been formulated long ago by Gibbs. At given pressure and temperature, for instance, it amounts to locating the global minimum of the total Gibbs free energy in thermodynamic state space. A necessary condition following from this is the equality of chemical potentials in all phases. For instance, for vapor–liquid equilibrium (VLE) of an n-component mixture:

$$\mu_i^{\mathrm{L}} = \mu_i^{\mathrm{V}} \qquad (i = 1, \ldots, n) \tag{1}$$

and

$$n_i^{\mathrm{V}} + n_i^{\mathrm{L}} = n_i^{\mathrm{F}} \qquad (i = 1, \ldots, n) \tag{2}$$

Here the superscripts L, V, and F denote liquid, vapor, and feed, respectively, and the $n_i^?$ are mole numbers. Equation (2) expresses the condition of material balance. Thus, to determine a phase split, these equations have to be solved for the unknowns n_i^{L} and n_i^{V}. The solution corresponds to a stationary point of the total Gibbs free energy and it has to be tested if this corresponds to a global (or if one is interested in meta-stable states local) minimum. In this paper we assume that the thermodynamic model contains some small parameter ε, such as, for instance, may arise through the addition of extra terms to an existing model or through the numerical smallness of certain model parameters. The effect of this small parameter can, at least formally, be determined by means of a perturbation expansion. There are several possible motivations to investigate and carry out such an expansion. In some cases the "unperturbed" ($\varepsilon = 0$) model will lead to a simplified set of equations, so that the perturbation expansion is a good alternative to arrive at the solution, which may be more attractive for computational reasons, or even the only way to arrive at an (approximate) solution at all. The perturbation series may also be used as a theoretical tool, to investigate the influence of certain parameters or model modifications on the solution (sensitivity analysis).

The idea of a perturbation approach is, of course, not new and in fact its applications abound in all branches of the natural sciences. Also, in the field of phase equilibria it has been used [1, 2]. The aim of this paper is, however, to derive the form of the perturbation expansion as it holds in general for problems in phase equilibria. As an example we apply it to multicomponent mixtures described by an equation of state with small binary parameters.

2. GENERAL PERTURBATION EXPANSION FOR PHASE EQUILIBRIUM EQUATIONS

In this section we derive the form of the equations describing phase equilibrium resulting from the perturbation expansion. Thus we assume that the thermodynamic model used, and hence the chemical potential, contains a small parameter ε. As a consequence, the solution of the phase equilibrium equations will also depend on ε. We assume that it can—at least formally—be expanded in powers of ε. Thus we write

$$n_i^\gamma = n_i^\gamma(\varepsilon) = \sum_{k=0}^{\infty} n_{ik}^\gamma \varepsilon^k \tag{3}$$

$$p = p(\varepsilon) = \sum_{k=0}^{\infty} p_k \varepsilon^k \tag{4}$$

$$T = T(\varepsilon) = \sum_{k=0}^{\infty} T_k \varepsilon^k \tag{5}$$

in which the superscript γ labels the phase. As we do not treat a specific phase equilibrium problem, at this stage, we treat all variables as depending on ε. However, for an isothermal flash calculation, for example, the pressure p and temperature T are actually given constants. The chemical potential now depends on ε both explicitly and implicitly, i.e., through composition, pressure, and temperature. We may expand it in powers of ε:

$$\mu_i = \sum_{k=0}^{\infty} \frac{1}{k!} \left(\frac{d^k \mu_i}{d\varepsilon^k} \right)_0 \varepsilon^k \tag{6}$$

in which the symbol $d/d\varepsilon$ stands for the total derivative with respect to ε and the subscript 0 implies that the quantity has to be evaluated at $\varepsilon = 0$. We restrict ourselves to two-phase equilibrium, for convenience denoted as vapor (V) and liquid (L), and require the condition of material balance to be satisfied in each order exactly, i.e.,

$$n_{i0}^{\mathrm{L}} + n_{i0}^{\mathrm{V}} = n_{i0}^{\mathrm{F}} \tag{7}$$

and

$$n_{ik}^{\mathrm{L}} + n_{ik}^{\mathrm{V}} = 0 \qquad (k = 1, 2, \ldots) \tag{8}$$

If we now substitute the perturbation expansion into Eq. (1) and equate the coefficients of all powers of ε to zero, we obtain a hierarchy of equations:

$$\mu_{i0}^{\mathrm{L}} = \mu_{i0}^{\mathrm{V}} \qquad \text{(“unperturbed” system)} \tag{9}$$

$$A\vec{q}^{\,(k)} - p_k \vec{v} - T_k \vec{w} = \vec{r}^{\,(k)} \tag{10}$$

in which A is a $n \times n$ matrix and $\vec{q}^{\,(k)}$, $\vec{v}$, and $\vec{w}$ are n-vectors with elements

$$A_{ij} = \left(\frac{\partial \mu_i}{\partial n_j}\right)_0^{\mathrm{L}} + \left(\frac{\partial \mu_i}{\partial n_j}\right)_0^{\mathrm{V}} \tag{11}$$

$$v_i = \Delta\left(\frac{\partial \mu_i}{\partial p}\right)_0; \qquad w_i = \Delta\left(\frac{\partial \mu_i}{\partial T}\right)_0; \qquad q_i^{(\mathrm{k})} = n_{ik}^{\mathrm{L}} = -n_{ik}^{\mathrm{V}} \tag{12}$$

and the elements of the vector $\vec{r}^{\,(k)}$ can be calculated in each order k from the results of the previous corrections. The symbol Δ denotes taking the difference between the two phases: $\Delta Q = Q^{\mathrm{V}} - Q^{\mathrm{L}}$. The expressions for $r_i^{(k)}$ in the two lowest orders are

$$r_i^{(1)} = \Delta\left(\frac{\partial \mu_i}{\partial \varepsilon}\right)_0 \qquad \text{(first order)} \tag{13}$$

and

$$\begin{aligned} r_i^{(2)} = \Delta \Bigg\{ & \frac{1}{2}\left(\frac{\partial^2 \mu_i}{\partial \varepsilon^2}\right)_0 + \sum_j \left(\frac{\partial^2 \mu_i}{\partial n_j\, \partial \varepsilon}\right)_0 q_j^{(1)} + \frac{1}{2} p_1 \sum_j \left(\frac{\partial^2 \mu_i}{\partial n_j\, \partial p}\right)_0 q_j^{(1)} \\ & + \frac{1}{2} T_1 \sum_j \left(\frac{\partial^2 \mu_i}{\partial n_j\, \partial T}\right)_0 q_j^{(1)} + \frac{1}{2} \sum_j \sum_k \left(\frac{\partial^2 \mu_i}{\partial n_j\, \partial n_k}\right)_0 q_j^{(1)} q_k^{(1)} \\ & + \left(\frac{\partial^2 \mu_i}{\partial p\, \partial \varepsilon}\right)_0 p_1 + \left(\frac{\partial^2 \mu_i}{\partial T\, \partial \varepsilon}\right)_0 T_1 + \frac{1}{2}\left(\frac{\partial^2 \mu_i}{\partial p^2}\right)_0 p_1^2 \\ & + \left(\frac{\partial^2 \mu_i}{\partial p\, \partial T}\right)_0 T_1 p_1 + \frac{1}{2}\left(\frac{\partial^2 \mu_i}{\partial T^2}\right)_0 T_1^2 \Bigg\} \qquad \text{(second order)} \end{aligned} \tag{14}$$

The zero-order equation (9), is the equation for the “unperturbed” system, which results from substitutions of $\varepsilon = 0$ into the original equation (1). This is, in general, still a set of coupled nonlinear equations, which, however, may be much simpler to solve due to the vanishing of ε. The other equations (10) are all linear and involve the same $n \times n$-matrix A in each order k; this matrix can be calculated from the solution of the “unperturbed” ($\varepsilon = 0$) problem alone. The same holds for $\vec{v}$ and $\vec{w}$. In each order we have to solve the linear system of equations (10) in which q_i (we drop the superscript k), p_k, and T_k are the unknowns. Since there are two unknowns more than equations, two extra relations have to be specified, corresponding to the type of phase equilibrium calculation one wants to perform. For instance, for an isothermal flash calculation, p_k and T_k vanish. For a saturation-point calculation the situation is a little more complicated. At such a point, which lies at the phase envelope (binodal), the amount of material in the incipient phase γ is infinitesimally small, and hence also the q_i. Taking the limit $n^\gamma \to 0$ in Eq. (10) we observe

$$\sum_j A_{ij} q_j = \sum_j \left\{ \frac{1}{n^{\mathrm{L}}} \left(n \frac{\partial \mu_i}{\partial n_j} \right)^{\mathrm{L}} + \frac{1}{n^{\mathrm{V}}} \left(n \frac{\partial \mu_i}{\partial n_j} \right)^{\mathrm{V}} \right\} q_j \to \sum_j \left(n \frac{\partial \mu_i}{\partial n_j} \right)^{\gamma} \hat{q}_j \equiv \sum_j \hat{A}_{ij}^{\gamma} \hat{q}_j \tag{15}$$

where $\hat{q}_i \equiv \lim(q_i/n^\gamma)$, remains finite at the phase envelope. Hence, for a saturation-point calculation the correction equations are of the form of Eq. (10) with A replace by $\hat{A}^\gamma$, and q_i by $\hat{q}_i$, which have to satisfy

$$\sum_i \hat{q}_i = 0 \tag{16}$$

so that one extra relation must be specified, which will usually be of the form

$$\alpha T_k + (1 - \alpha) p_k = 0 \tag{17}$$

where $\alpha \in [0, 1]$ is constant. We note that, since $\hat{A}_\gamma$ is an intensive matrix, $\vec{x}^\gamma \cdot \hat{A}_\gamma = 0$, where $\vec{x}^\gamma$ is the composition vector for the incipient phase γ. If we therefore multiply Eq. 10) with this vector on the left, we obtain

$$(\vec{x}^\gamma \cdot \vec{v})\, p_k + (\vec{x}^\gamma \cdot \vec{w})\, T_k + (\vec{x}^\gamma \cdot \vec{r}^{(k)}) = 0 \tag{18}$$

From this and Eq. (17), p_k and T_k can be calculated first and substituted into Eq. (10). The $\hat{q}_i$ then follow as the solution from Eq. (10) under the restriction given by Eq. (16). This is a soluble system, since $\operatorname{rank}(\hat{A}^\gamma) = n - 1$.

Without loss of generality we may put the total amount of moles n^{F} to be unity, which we do hereafter. In that case $n^{\mathrm{L}} = \phi$ is the liquid fraction ("liquid-to-feed ratio"), and similarly, $n^{\mathrm{V}} = 1 - \phi$ is the fraction vaporized. In each order k, the solution of Eq. (10) gives rise to corrected values of the liquid fraction,

$$\delta\phi = \sum_j q_j \tag{19}$$

and of the mole fractions in the coexisting phases,

$$x_{i,\text{new}}^{\text{L}} = \frac{\phi x_{i,\text{old}}^{\text{L}} + q_i}{\phi + \delta\phi} \tag{20}$$

$$x_{i,\text{new}}^{\text{V}} = \frac{(1-\phi) x_{i,\text{old}}^{\text{V}} - q_i}{1 - \phi - \delta\phi} \tag{21}$$

For saturation-point calculations $\delta\phi = 0$ and the correction equations simplify to

$$x_{i,\text{new}}^{\gamma} = x_{i,\text{old}}^{\gamma} + \sigma^{\gamma} \hat{q}_i \tag{22}$$

where $\sigma^{\text{L}} = 1$ (bubble-point calculation) and $\sigma^{\text{V}} = -1$ (dew-point calculation).

The matrix A in Eq. (11) plays an important role in the perturbation expansion. We note that the same matrix occurs in the Newton–Raphson step equations of the unperturbed system. These equations are in fact identical in form to Eq. (10), but with a different right-hand side, which becomes the differences of the chemical potentials themselves between the two phases. With the right-hand side equal to zero, Eq. (10) relates solutions at neighboring points in thermodynamic state space. This can be used to generate initial estimates from the solution in a neighboring point.

The phase envelope of the unperturbed system will, in general, differ from the actual phase envelope. This means that there will be regions in which a phase split occurs but which will be single-phase regions for $\varepsilon = 0$, and vice versa. This problem can be overcome, however, by extending the two-phase region of the unperturbed problem mathematically by allowing for unphysical values of the liquid fraction ϕ, outside the interval $[0, 1]$. The corrected value of ϕ will then lie within this interval. The reverse may also be the case, i.e., that the value of ϕ becomes unphysical after correction, indicating a single-phase point.

We have presented the general perturbation scheme using pressure, temperature, and composition as basic variables, which are used in most practical applications. It is possible to use other variables, for instance, volume instead of pressure, and derive the corresponding perturbation expansion [1]. The perturbation approach can also be applied to the spinodal equations. The condition for a point to lie on the spinodal curve is $\lambda = 0$, where λ is the smallest eigenvalue of $\hat{A}$. This eigenvalue can also be expressed as a series in ε. The terms in this series can be evaluated using the Rayleigh–Schroedinger perturbation theory, known from quantum mechanics.

3. THE UNPERTURBED SYSTEM

For the perturbation method to be useful, the thermodynamic model must contain a small parameter ε, such that for $\varepsilon = 0$ the phase equilibrium equations can be solved more easily. The hypothetical physical system described through the equations with $\varepsilon = 0$, with its own phase diagram, is referred to as the unperturbed system. We mention two ways in which a small parameter can enter the equations. One possibility is through the overall (feed) composition $\vec{z}$:

$$\vec{z} = \vec{z}_0 + \varepsilon \vec{z}_1 \tag{23}$$

where $\vec{z}_0$ may be the composition vector for a mixture with a fewer number of components. To justify the perturbation expansion in this case, the assumption must be made that Eq. (23), with the second term much smaller than the first, holds in both coexisting phases. With this type of ansatz Morrison and Kincaid [1] have studied the phase behavior of a mixture of a pure solvent and a small amount of polydisperse material. The other possibility is through the molecular parameters of the model, by writing any k-particle property Q as the sum of an unperturbed part and a perturbation:

$$Q(i_1,..., i_k) = Q_0(i_1,..., i_k) + \varepsilon Q_1(i_1,..., i_k) \tag{24}$$

(in applications, k will rarely exceed 2), with Q_0 corresponding to the unperturbed system. In this formula it is convenient to define the scale of Q_1 such that ε equals unity. The expansion in ε is then effectively an expansion in Q_1, so that ε is just a bookkeeping parameter. The property Q will enter the thermodynamic model through its composition-averaged value:

$$\langle Q \rangle = \sum_{\{i_l\}} x_{i_1} \cdots x_{i_k} Q(i_1,..., i_k) \tag{25}$$

or a similar sum. Of course, a division as in Eq. (24) can be done in various ways. However, we dispose of a guiding principle, through which we can achieve that not only the equations of the unperturbed system, but also the correction equations are simplified. This principle lies in the following theorem [3]: if the nontrivial part of the Gibbs free energy function $G - RT \sum x_i \log x_i$ depends upon composition only through a set of K scalar products

$$B_l = (\vec{x} \cdot \vec{\beta}_l) \qquad (l = 1,..., K) \tag{26}$$

then (i) the corresponding two-phase equilibrium equations can be reduced to a set of, at most, $K+1$ equations in $K+1$ unknowns; and (ii) the correction equations (10) can be reduced to a linear system of size $\leqslant K+1$. For the proof we refer to Ref. 2. To employ this principle, we must ensure that, for the unperturbed system, the conditions of the theorem apply with $K \ll n$. How to achieve this depends, of course, on the model, but there are some general possibilities. For example, we may take Q_0 as a product of k one-particle properties:

$$Q_0(i_1,..., i_k) = \prod_{l=1}^{k} \eta_{i_l} \qquad \text{(factorization method)} \tag{27}$$

This makes sense, of course, only if the deviation from the actual value is (uniformly) small. Each parameter Q gives rise to a single scalar product B, with $\beta_i = \eta_i$ in Eq. (26). Another general method is the family approach, in which the species are divided among a (small) number of families Ω_s $(s = 1,..., k)$ and Q_0 is taken to depend only on the family labels:

$$Q_0(i_1,..., i_k) = F[s(i_1),..., s(i_k)] \qquad \text{(family method)} \tag{28}$$

where $F(s_1,..., s_k)$ is a k-family property. For notational convenience we have introduced the family indicator function $s(i)$, which specifies the label of the family to which species i belongs. For each Q and each family there is one scalar product B_s, with $\beta_{s,i} = \delta_{s,s(i)}$ (Kronecker symbol) in Eq. (26). The function F in (28) must be chosen such as to minimize the $Q - Q_0$ in an appropriate sense. It may, for instance, be taken to be the feed family-averaged value of Q:

$$F(s_1,..., s_k) = \sum_{i_m \in \Omega_{s_m}} z_{i_1} \cdots z_{i_k} Q(i_1,..., i_k) \tag{29}$$

This is actually what is used when lumping schemes or pseudocomponents are employed. To conclude this section we give a concrete example, which is worked out later. Consider a mixture described through a two-parameter equation of state with van der Waals-type mixing rules:

$$a = \sum_{i=1}^{n} \sum_{j=1}^{n} a_{ij} x_i x_j \tag{30}$$

and

$$b = \sum_{i=1}^{n} x_i b_i \tag{31}$$

The quantities a_{ij} and b_i correspond to the Q above. The b parameter is already a scalar product. We introduce the small parameter ε through the formula

$$a_{ij} = \sqrt{a_i a_j}(1 - \varepsilon\theta_{ij}) \tag{32}$$

where a_i is the value of the a parameter for the pure substance i, and θ_{ij} are the so-called interaction parameters, which are often numerically small. This makes the perturbation expansion feasible. The unperturbed system corresponds to a mixture with vanishing interaction coefficients. The scalar products in Eq. (26) are the equation-of-state parameters, so that $K = 2$. Indeed, it has been shown before by Michelsen [4] that the phase equilibrium equations can be simplified to a set of only three equations. This is an example of the factorization method. The family method can be applied here, too, by taking θ_{ij} zero within each family and constant between families, for the unperturbed system. The set of zero-order equations resulting from this has been derived in Ref. 5.

4. EXAMPLE: SMALL BINARY INTERACTION COEFFICIENTS

We have worked out the equations of the perturbation method for the example in the last section: multicomponent mixtures described through a two-parameter equation of state. The Gibbs free energy function for such a mixture is of the form

$$G = NRT\left\{\sum_{i=1}^{n} x_i \log x_i + g(a, b, p, T)\right\} \tag{33}$$

The chemical potential (per RT) resulting from this can be written as

$$\hat{\mu}_i \equiv \frac{\mu_i}{RT} = \log x_i + C_0 + C_1 e_i + C_2 b_i \qquad \text{with} \qquad e_i = \sum_{j=1}^{n} a_{ij} x_j \tag{34}$$

where the coefficients C_k can be expressed in g and its first-order partial derivatives. For the unperturbed system, for which $a_{ij} = \sqrt{a_i a_j}$, we introduce a $3 \times n$-matrix β with elements

$$\beta_{0i} = 1; \qquad \beta_{1i} = \sqrt{aa_i}; \qquad \beta_{2i} = b_i \tag{35}$$

so that the unperturbed chemical potential (per RT) can be written as

$$\hat{\mu}_{i0} = \log x_i + \sum_{l=0}^{2} C_l \beta_{li} \tag{36}$$

The computational advantage of using the unperturbed system lies in the fact that no multiple summations have to be performed repeatedly and that it is possible to reduce the equation system to a set of only three.

We now investigate the linear set of equations (10), which we write briefly as

$$A\vec{q} = \vec{R} \tag{37}$$

where the right-hand side is assumed to be known. These equations occur in three different places, each time with a different right-hand side: first, as the Newton–Raphson correction equations for the unperturbed system; second, as the equations relating composition, pressure, and temperature of neighboring states; and third, as the correction equations in the perturbation method. So if a Newton–Raphson method is used to solve the unperturbed equations, the final Jacobian matrix can also be used in the perturbation corrections and to generate initial conditions in a neighboring point. The fact that Eq. (37) can be simplified, as we show, in accordance with the theorem mentioned in Section 3, is therefore very useful. For saturation-point calculations, T_k and/or p_k must be calculated first [see below Eq. (15)]. The matrix in Eq. (37) is singular for that case, but this does not essentially change the following discussion. In general, the matrix A is a sum of contributions from both phases [see Eq. (11)]. These can be derived from differentiation of (Eq. (34) with respect to composition and substitution of $\varepsilon = 0$:

$$\hat{A}^{\gamma}_{ij} = \frac{\delta_{ij}}{x^{\gamma}_i} + \sum_{l=0}^{2} \sum_{m=0}^{2} C^{\gamma}_{lm} \beta_{li} \beta_{mj} \tag{38}$$

The coefficients C^{γ}_{lm} involve the first and second derivatives of g with respect to a and b. The complete matrix is therefore of the form

$$A = \Lambda + \tilde{\beta} C \beta \tag{39}$$

where Λ is a diagonal matrix with elements

$$\Lambda_{ii} = \frac{x^{\mathrm{F}}_i}{\phi(1-\phi)\, x^{\mathrm{L}}_i x^{\mathrm{V}}_i} \tag{40}$$

and

$$C = \frac{C^{\mathrm{L}}}{\phi} + \frac{C^{\mathrm{V}}}{1-\phi} \tag{41}$$

Substitution of Eq. (39) into Eq. (37) yields the relation:

$$\vec{q} = \Lambda^{-1}(\vec{R} - \tilde{\beta} C \beta \vec{q}) \tag{42}$$

which expresses $\vec{q}$ in the three-vector $\vec{s} \equiv \beta\vec{q}$, involving $\vec{q}$ itself. If we now multiply Eq. (42) with β from the left, we obtain an equation for $\vec{s}$:

$$S\vec{s} = RA^{-1}R \tag{43}$$

which involves the 3×3 matrix

$$S = I + \beta A^{-1}\tilde{\beta}C \tag{44}$$

The solution $\vec{s}$ must be substituted back into Eq. (42) to yield the solution of Eq. (37). Thus, Eq. (37) can indeed be reduced to a set of only three linear equations.

As an illustration, we give some numerical results. For a flash calculation of a 17-component mixture, we show the deviations in the liquid composition from the exact values in Table I, in zero, first, and second order. The Soave equation of state was used. The largest binary interaction coefficient was 0.15. The largest deviations observed are for CO_2, which has a relatively large interaction coefficient with most of the other components. By "exact values" we mean the values obtained from the exact solution of the complete flash equations. In Table II we give CPU

Table I. Flash Calculation for a 17-Component Mixture[a]

Compound	Unperturbed	First order	Second order	Exact value
Ni	0.28	−0.44	0.02	0.1014E−01
Methane	0.25	0.00	0.00	0.4235E+00
Ethane	−0.29	0.00	0.00	0.5797E−01
CO2	36.45	−6.00	0.60	0.1426E−01
H2S	8.56	−0.38	0.03	0.7130E−02
Propane	−0.70	0.00	0.00	0.3644E−01
i-Butane	−0.97	0.00	0.00	0.1095E−01
n-Butane	−1.06	0.01	0.00	0.2155E−01
i-Pentane	−1.32	0.02	0.00	0.1279E−01
n-Pentane	−1.38	0.02	0.00	0.1224E−01
n-Hexane	−1..65	0.05	0.00	0.2773E−01
Toluene	−1.56	0.29	−0.03	0.2460E−01
n-Octane	−1.94	0.12	−0.01	0.9593E−01
n-Undecane	−1.82	0.25	−0.02	0.1181E+00
n-Tetradecane	−1.54	0.32	−0.02	0.7289E−01
n-Heptadecane	−1.39	0.35	−0.03	0.3261E−01
n-Eicosane	−1.32	0.35	−0.03	0.2110E−01

[a] Liquid composition at $T = 350$ K and $p = 150$ bar; procentual deviations from the exact value in the various orders.

Table II. CPU Times for a Single Bubble-Point Pressure Calculation for a Multicomponent Mixture as a Function of the Number of Components n: Comparison of the Traditional Direct Substitution Method with the Perturbation Method (Up to Second-Order Correction Has been Applied)

n	Direct substitution (ms/iteration)	Zero order (ms/iteration)	Correction (ms)
20	0.5	0.5	1.0
30	0.9	0.6	1.6
40	1.5	0.7	2.4

times for a single bubble-point calculation as a function of the number of components in a (hypothetical) mixture, on an IBM 3090 mainframe. We compare the time needed for a single iteration in the traditional direct substitution method with that needed for a single iteration for the unperturbed system. We also give the time needed to obtain the correction up to second order. It is seen that the computation time per iteration increases only linearly with the number of components in the perturbation method, whereas it increases much faster in the direct substitution method. This effect is due to the multiple summations occurring in the mixing rules. The reader should realize that on top of this advantage, the number of iterations can be much lower in the perturbation method, especially near critical points, due to the quadratic convergence of the Newton–Raphson method. Solving the correction equations, which do contain multiple summations, takes more time but must be done only once. We have not applied any special acceleration procedures in both methods, in order to exhibit clearly the computational advantage of the perturbation method, which is the linear increase in computational effort with the number of components and the quadratic convergence.

If a given mixture contains some components whose interaction coefficients cannot be neglected, it is still possible to apply the method described here, by chosing the unperturbed system such that only the other binary interaction coefficients vanish. How this can be done in a systematic way has been described in Ref. 3 (see also Ref. 6). If there are L "special" components, the dimensionality of the unperturbed system will become $2L+3$ (rather than three). By a judicious choice of these special components, a balance between accuracy and computation time is achieved. Note that if the remaining interaction coefficients are very small, first-order correction will suffice.

In practice, of course, what is needed, especially in large problems, is a fast and robust algorithm (or combination of algorithms) involving initialization procedures, stability tests (accelerated), direct substitutions, Newton–Raphson iterations, etc. In each subprocedure advantage can be taken of the special structure of the zero-order problem. Therefore in general it will be possible to find a value *n* beyond which the perturbation method leads to computational savings (at the cost of some loss of accuarcy). We expect that it will offer an attractive alternative, especially in very large problems. In a process simulator, for instance, a possible strategy is first to carry out a complete simulation with $\varepsilon = 0$ and then to apply the corrections (in each unit).

5. CONCLUSION

We have presented a general scheme for the solution of phase equilibrium equations by means of a perturbation expansion, together with a method to find a suitable zero-order system. It may be used to obtained approximate solutions to difficult problems or to investigate the influence of certain model parameters on the solution. The example of multicomponent mixtures described by a two-parameter equation of state with small binary interaction coefficients shows that it can also be used to reduce computational effort, if the number of compounds *n* is large enough.

The perturbation method naturally divides into two parts: the solution of the zero-order problem and the evaluation of the correction. The zero-order problem must be simpler to solve than the full problem. To obtain the correction in each order a set of *n* linear equations has to be solved. However, if the zero-order system is chosen according to the described method, the dimensionality of this set can reduced to a small number, independent of *n*. The same reduction applies to the zero-order system itself.

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