A Quantum Cluster Equilibrium Theory for Multi-Component Liquids

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Abstract

In this work, we present a new theory to treat multi-component liquids based on quantum-chemically calculated clusters. The starting point is the binary quantum cluster equilibrium theory that is able to treat binary systems. The theory provides one equation with two unknowns. In order to obtain another linearly independent equation, conservation of mass is used. However, increasing the amount of components leads to more unknowns and this requires linearly independent equations. We address this challenge by introducing a generalization of the conservation of arbitrary quantities, accompanied by a comprehensive mathematical proof. Furthermore, a case study for the application of the new theory to ternary mixtures of chloroform, methanol and water is presented. Calculated enthalpies of vaporization for the whole composition range are given, and populations or weights of the different clusters are visualized.

1 Introduction

The chemical industry has demand for accurate predictions of thermodynamic properties of liquid mixtures.^{1,2} Various methods exist to accommodate this demand, such as the quantum-chemical solvent model COSMO-RS^{3,4} as well as the group contribution methods UNIQUAC⁵ and its functional-group extension UNIFAC.⁶ Today, classical molecular dynamics (MD) simulations, known for their computational efficiency, are routinely employed to determine the thermodynamic and physico-chemical properties of liquids. These simulations can be applied to study a diverse array of systems, relying on the underlying force field. Calculating thermodynamic properties from MD simulations is a very active research field, with new methods and approaches being developed and benchmarked regularly. $^{7-12}$ In the standard formulation of MD, the intra- and intermolecular interactions are described by pairwise additive Lennard-Jones (LJ) and a Coulomb potentials. In many commonly used force fields, the LJ potential is parameterized to reproduce experimentally obtained properties of the pure components. When extending the simulated systems from pure liquids to multi-component systems, the multi-component properties are often calculated by averaging over the properties of the pure components.¹³ In such cases, the LJ parameters are usually averaged either geometrically or arithmetically (Lorentz–Berthelot mixing rules¹⁴) to obtain the LJ parameters of the mixture. This is computationally fast, but it might lead to inaccurate results, especially when the LJ parameters of the pure components differ significantly,^{15,16} and the inclusion of correction terms might be necessary to accurately calculate certain properties such as diffusion coefficients.¹⁷ To avoid such inaccuracies and the need for further parameterization, ab initio MD (AIMD) simulations present a highly accurate albeit computationally demanding alternative.^{18,19} Early examples of AIMD works date back to the 70s,^{20,21} and first applications to condensed phases were published by the late 80s.^{22,23} Although continuous advances in computational power make AIMD an increasingly feasible option,^{24,25} limiting factors such as the system size and number of simulations hamber the sampling of a wide range of concentrations and temperatures.

One fundamentally different approach to describe liquids and their mixtures is offered by the quantum cluster equilibrium (QCE) method.^{26,27} It was developed by Frank Weinhold and is conceptually based on the idea that the liquid bulk system can be described as a dense distribution of statistically reoccurring molecular cluster motifs. Within the framework of the QCE method, a cluster is defined as a characteristic configuration of molecules that exists in-between the limits of an isolated monomer in the gaseous phase and a large aggregate in the condensed phase. Through a combination of statistical mechanics and quantumchemical calculations, the QCE method can be used to determine populations for a set of representative clusters and, thus, build a cluster-based model of liquids and gases. Through weighting the partition function of each cluster by its population, the total system partition function can be obtained, allowing the direct calculation of thermodynamic properties such as enthalpy or heat capacity. The QCE method has been successfully applied to study pure liquids, molecular mixtures, and ionic liquids.^{26,28–40}

The geometry and interaction energies of each cluster in a cluster set are quantumchemically optimized. A key advantage of the QCE method is that highly accurate quantumchemical methods can be applied to these clusters up to coupled cluster theory (CC)^{41,42} and others. Additionally, QCE allows for the inclusion of different cluster sizes and compositions. It yields weights for the clusters that outperform simple conformer weighting as is done in standard quantum chemical calculations when bulk phase quantities need to be accessed.⁴³ However, due to its inherently static description of the system, the QCE method is not able to access dynamic properties (e.g., diffusion coefficients) as is done in MD simulations, but needs additional approximations.

Up to now, the QCE theory has been limited to binary systems (bQCE),⁴⁴ i.e., systems

consisting of two different types of molecules, allowing the study of binary mixtures or ionic liquids. Noting the existing demand for accurate predictions of thermodynamic properties of systems with more than two components, a generalization of the QCE theory to multicomponent systems is highly desirable. In this work, we present a new theory to describe multi-component systems within the QCE framework (mQCE) and provide a mathematical proof for its central equations. The new theory overcomes the previous requirement for conserved quantities to solve the central equation system for the cluster populations. Thus, it allows the inclusion of an arbitrary number of components. Furthermore, by eliminating the cluster mass as a quantity in the new equations presented herein, the study of components with equal or near equal mass is possible, such as racemic mixtures or ionic liquids with an anion and cation of similar mass.

This paper is outlined as follows: basic equations from thermochemistry are recapitulated in the Supporting Information, forming the foundation of the binary QCE formalism introduced in section 2.1 and followed by the extension to multi-component systems in section 2.2. Computational details and a case study for the application of the mQCE theory are given in sections 3 and 4, respectively.

2 Methodology

The underlying theory of the QCE method was initially published by Frank Weinhold in 1998.²⁷ While the QCE theory was originally developed for the description of pure liquids and implemented in the PEACEMAKER⁴⁵ software in 2005,⁴⁶ it was extended to binary mixtures of liquids by our group in 2011.⁴⁴

2.1 Binary QCE theory

The bQCE formalism is summarized in the following. For a more detailed derivation, we refer the reader to Ref. 44. In the bQCE method, every particle exists either in the monomeric ground state or as part of a cluster. Here, a cluster consists of one or more monomers from one (in case of a neat system) or two (in case of a binary mixture) components. The number of cluster states that a particle can exist in is limited to a selection of representative quantum-chemically optimized clusters that together form the so-called cluster set. The ensemble is assumed to be in thermodynamic equilibrium, that is, the clusters form and dissociate according to

$$nA + mB \rightleftharpoons A_n B_m,$$
 (1)

where A and B denote the monomers of components a and b, respectively. To generalize the above notation, a cluster of the form $A_n B_m$ will be given the general label P_i , where $i \in \{1, \ldots, L\}$ is a running index to differentiate between each unique representative cluster, and L is the number of clusters in the cluster set. Equation (1) can then be expressed in a more general way as

$$n_i^a \mathbf{A} + n_i^b \mathbf{B} \rightleftharpoons \mathbf{P}_i,$$
 (2)

where n_i^a and n_i^b are the number of monomers of components a and b in the cluster P_i , respectively $(n_i^a, n_i^b \in \mathbb{N}_0, \text{ with } \mathbb{N}_0 \text{ being the set of natural numbers including zero})$. By introducing this notation, multiple clusters of identical composition (but composed of max. two components) can exist, taking into account different conformers and molecular arrangements of the monomers.

The initial goal is to determine the distribution $\{N_i\}$ (with $N_i \in \mathbb{N}_0$) of clusters P_i that, at a given state of volume V, temperature T, and total number of particles \mathcal{N}^{tot} , represents a minimum of the free energy F:

$$F = -k_{\rm B}T\ln Q. \tag{3}$$

It should be noted that \mathcal{N}^{tot} is the sum of the total numbers of monomers of the two

components $\mathcal{N}_1^{\text{tot}}$, $\mathcal{N}_2^{\text{tot}}$. The system partition function Q is given by

$$Q = \prod_{i}^{L} \frac{1}{N_i!} q_i^{N_i},\tag{4}$$

where q_i and N_i are the partition function and population of cluster P_i , and L is the total number of clusters, respectively. The cluster partition function can be written as a product of partition functions associated with the clusters degrees of freedom:

$$q = q^{\text{trans}} q^{\text{rot}} q^{\text{vib}} q^{\text{elec}},\tag{5}$$

where q^{trans} , q^{rot} , and q^{vib} are the translational, rotational, and vibrational cluster partition functions and are calculated using standard models of statistical thermodynamics (see SI).

The electronic cluster partition q^{elec} is calculated from the adiabatic interaction energy of the monomers upon cluster formation, $\Delta_{\text{bind}} \varepsilon_i^{\text{elec}}$:

$$\Delta_{\text{bind}}\varepsilon_i^{\text{elec}} = \varepsilon_i^{\text{elec}} - n_i^a \varepsilon_1^{\text{elec}} - n_i^b \varepsilon_2^{\text{elec}},\tag{6}$$

where $\varepsilon_i^{\text{elec}}$ is the electronic energy of cluster P_i . To account for interaction between the clusters, an additional (attractive) mean-field term is added to the cluster partition function:

$$q_i^{\text{elec}} = \exp\left\{-\frac{\Delta_{\text{bind}}\varepsilon_i^{\text{elec}} - (n_i^a + n_i^b)\frac{a_{\text{mf}}}{V}}{k_{\text{B}}T}\right\},\tag{7}$$

using the empirical mean-field parameter $a_{\rm mf}$ with the dimension energy volume. The mean-field contribution to the electronic partition function is proportional to the cluster size and the density of the system. The $a_{\rm mf}$ parameter is a simple approach to scale the strength of the mean-field.

Moreover, to account for the eigenvolume v_i of the clusters, that is inaccessible to translation, the exclusion volume V_{ex} is introduced. Available methods to calculate the cluster volume, such as the GEPOL⁴⁷ algorithm, are often sensitive to the choice of atomic radii.²⁶ This requires an additional (dimensionless) empirical parameter b_{xv} , in order to scale the cluster volumes correctly:

$$V_{\rm ex} = b_{\rm xv} \sum_{i}^{L} N_i v_i \tag{8}$$

Different approaches to implement a temperature dependence of b_{xv} were explored in the past, ^{48,49} but will not be included here. Following this, the translational partition function of the clusters is modified to

$$q_i^{\text{trans}} = \frac{V - V_{\text{ex}}}{\Lambda^3}.$$
(9)

At this point, eqs. (7) and (9) can be combined with $q_i^{\text{vib,rot}}$ (cf. Supporting Information) to yield the cluster partition function q_i and ultimately, the system partition function Q(eq. (4)). To calculate the partition function in practice, and yield thermodynamic data, the characteristic quantities of the canonical ensemble $(\{N_i\}, V, T)$ as well as the empirical parameters a_{mf} and b_{xv} have to be determined. The parameters a_{mf} and b_{xv} are conceptually equivalent to the parameters a and b in the van der Waals equation of state, respectively, in that they account for the attractive force between particles as well as their volume. A more detailed demonstration of this connection can be found in the Supporting Information.

In terms of the canonical ensemble quantities, we start from the conservation of particles, serving as an integral physical constraint of this ensemble:

$$\mathcal{N}_1^{\text{tot}} + \mathcal{N}_2^{\text{tot}} = \sum_i^L (n_i^a + n_i^b) N_i, \qquad (10a)$$

$$0 = \sum_{i}^{L} \frac{(n_i^a + n_i^b)N_i}{\mathcal{N}_1^{\text{tot}} + \mathcal{N}_2^{\text{tot}}} - 1,$$
(10b)

$$0 = \sum_{i}^{L} \tilde{N}_i - 1. \tag{10c}$$

It should be noted that, in the above equation, $\mathcal{N}_1^{\text{tot}}$ and $\mathcal{N}_2^{\text{tot}}$ denote the total numbers of

monomers of the components 1 and 2, respectively. We further note that, as QCE calculations are in practice performed with $\mathcal{N}^{tot} \approx 1$ mol, the quantities \mathcal{N}_1^{tot} and \mathcal{N}_2^{tot} are not fractional, but integer numbers. Additionally, the monomer-normalized populations \tilde{N}_i are introduced. \tilde{N}_i is the relative population of cluster *i*, normalized to the number of monomers and relevant for the visualization of the cluster distribution in following sections of this work. We note that \tilde{N}_i are fractional numbers between zero and one. With the system being in equilibrium, any change in the free energy *F* due to infinitesimal changes in any cluster populations $\{N_i\}$ must be balanced by infinitesimal changes in the monomer populations:

$$\frac{\partial F}{\partial N_i} = n_i^a \; \frac{\partial F}{\partial N_1} + n_i^b \; \frac{\partial F}{\partial N_2}.$$
(11)

Using eq. (4) and

$$\ln Q = \ln \left(\prod_{i}^{L} \frac{1}{N_i!} q_i^{N_i} \right) \tag{12a}$$

$$=\sum_{i}^{L} \left(N_{i} \ln q_{i} - \ln N_{i}!\right)$$
(12b)

eq. (11) can be rearranged to

$$\frac{\partial}{\partial N_i} \sum_{i}^{L} (N_i \ln q_i - \ln N_i!) = n_i^a \left(\frac{\partial}{\partial N_1} \sum_{i}^{L} (N_i \ln q_i - \ln N_i!) \right) + n_i^b \left(\frac{\partial}{\partial N_2} \sum_{i}^{L} (N_i \ln q_i - \ln N_i!) \right).$$
(13)

Employing the *Stirling* formula to approximate $\ln(N_i!)$, eq. (13) can be solved to show the relation between all cluster populations and the monomer populations. As aforementioned, QCE calculations are performed for particle numbers in the range of 10^{23} , such that any significantly populated cluster will satisfy the requirement of a large N_i in view of the *Stirling*

approximation. Equation (13) can thus be simplified to:

$$\ln \frac{q_i}{N_i} = n_i^a \ln \frac{q_1}{N_1} + n_i^b \ln \frac{q_2}{N_2},$$
(14a)

$$N_i = q_i \left(\frac{N_1}{q_1}\right)^{n_i^a} \left(\frac{N_2}{q_2}\right)^{n_i^b}.$$
(14b)

It should be noted that the above equation reduces the problem of finding the entire set of cluster populations $\{N_i\}$ to finding the monomer populations N_1 and N_2 . By inserting eq. (14b) into eq. (10b) the *population polynomial*,⁵⁰ one of the key ingredients of the bQCE theory is obtained:

$$0 = \sum_{i}^{L} \frac{n_{i}^{a} + n_{i}^{b}}{\mathcal{N}_{1}^{\text{tot}} + \mathcal{N}_{2}^{\text{tot}}} \cdot q_{i} \left(\frac{N_{1}}{q_{1}}\right)^{n_{i}^{a}} \left(\frac{N_{2}}{q_{2}}\right)^{n_{i}^{b}} - 1.$$
(15)

The number of unknowns in this expression equals two (the number of components in the system) and hence, a second equation is needed: the conservation of mass, given by

$$m_1 \mathcal{N}_1^{\text{tot}} + m_2 \mathcal{N}_2^{\text{tot}} = \sum_i^L (n_i^a m_1 + n_i^b m_2) N_i,$$
 (16a)

$$0 = \sum_{i}^{L} \frac{n_i^a m_1 + n_i^b m_2}{m_1 \mathcal{N}_1^{\text{tot}} + m_2 \mathcal{N}_2^{\text{tot}}} N_i - 1, \qquad (16b)$$

where m_1 and m_2 are the molecular weights of the two components. It should be noted that eq. (16b) is simply the mass-weighted form of eq. (10b). Inserting eq. (14b) into eq. (16b) yields the mass polynomial:

$$0 = \sum_{i}^{L} \frac{n_{i}^{a} m_{1} + n_{i}^{b} m_{2}}{m_{1} \mathcal{N}_{1}^{\text{tot}} + m_{2} \mathcal{N}_{2}^{\text{tot}}} \cdot q_{i} \left(\frac{N_{1}}{q_{1}}\right)^{n_{i}^{a}} \left(\frac{N_{2}}{q_{2}}\right)^{n_{i}^{b}} - 1.$$
(17)

At this point, it is worth noting that the derived equations allow the calculation of the partition function at *any* temperature, but only for a given volume. Therefore, the volume is to be expressed as a function of the cluster populations. We start from the definition of

the pressure p that can be derived from the free energy as

$$p = -\frac{\partial F}{\partial V},$$

$$0 = -p + k_{\rm B}T \frac{\partial \ln Q}{\partial V}.$$
(18)

Keeping the contributions to Q from different degrees of freedom in mind, only translational and electronic contributions to the partition function depend on the volume. The other degrees of freedom vanish during the derivation. Upon inserting eq. (12) into eq. (18) and subsequent rearranging, the *volume polynomial* is obtained:

$$0 = -pV^{3} + \left(\sum_{i}^{L} k_{\rm B}TN_{i} + pV_{\rm ex}\right)V^{2} - \left(\sum_{i}^{L} N_{i}(n_{i}^{a} + n_{i}^{b})a_{\rm mf}\right)V + \sum_{i}^{L} N_{i}(n_{1}^{a} + n_{2}^{b})a_{\rm mf} \cdot V_{\rm ex}.$$
(19)

Since both the population and volume polynomial depend on the monomer populations and the volume V, an iterative procedure is applied in practice: For a given set of T, a_{mf} and b_{xv} , the monomer populations are calculated for the first time using an initial volume guess. From that, volume and monomer populations are calculated in an iterative and self-consistent fashion. Doing so, the bQCE theory is fully defined and can be applied to any system of interest.

2.2 Multi-component QCE theory

Building up on the binary QCE theory, the multi-component QCE theory is derived. Some equations can be extended straightforwardly. The chemical reaction of cluster formation in a multi-component system with K different components is given by

$$\sum_{c}^{K} n_{i}^{c} \mathcal{C} \longleftrightarrow \mathcal{P}_{i}, \tag{20}$$

where n_i^c is the number of monomers C of the general component c with $c \in \{1, \ldots, K\}$ that form the cluster P_i , $i \in \{1, \ldots, L\}$ is an index to differentiate between each unique representative cluster, and L is the number of representative clusters in the cluster set. In the following, the monomer of each component has the index i = c, that is, P_1, P_2, \ldots, P_K denote the monomers of each component, respectively. By adjusting the expression of the adiabatic interaction energy

$$\Delta_{\text{bind}}\varepsilon_i^{\text{elec}} = \varepsilon_i^{\text{elec}} - \sum_c^K n_i^c \varepsilon_c^{\text{elec}},\tag{21}$$

the electronic partition function can easily be extended to multi-component systems:

$$q_i^{\text{elec}} = \exp\left\{-\frac{\Delta_{\text{bind}}\varepsilon_i^{\text{elec}} - \sum_c^K n_i^c \frac{a_{\text{mf}}}{V}}{k_{\text{B}}T}\right\}.$$
(22)

Conservation of the total number of monomers $\mathcal{N}_c^{\text{tot}}$ of each component is generalized by

$$\sum_{c}^{K} \mathcal{N}_{c}^{\text{tot}} = \sum_{i}^{L} \sum_{c}^{K} n_{i}^{c} N_{i},$$
$$0 = \frac{\sum_{i}^{L} \sum_{c}^{K} n_{i}^{c} \cdot N_{i}}{\sum_{c}^{K} \mathcal{N}_{c}^{\text{tot}}} - 1 = \sum_{i} \tilde{N}_{i} - 1.$$
(23)

Similar to the bQCE theory, changes in the free energy with respect to the monomer populations obey to the following condition:

$$\frac{\partial F}{\partial N_i} = \sum_{c}^{K} n_i^c \; \frac{\partial F}{\partial N_c}.$$
(24)

Following the derivation presented in eqs. (11) to (14), we obtain a multi-component relation between the cluster populations and the monomer populations:

$$N_i = q_i \prod_c \left(\frac{N_c}{q_c}\right)^{n_i^c}.$$
(25)

This equation can then be transformed into the generalized population polynomial by inserting eq. (25) into eq. (23):

$$0 = \frac{1}{\sum_{c}^{K} \mathcal{N}_{c}^{\text{tot}}} \sum_{i}^{L} \sum_{c}^{K} \left\{ n_{i}^{c} \cdot \prod_{c} \left[q_{i} \left(\frac{N_{c}}{q_{c}} \right)^{n_{i}^{c}} \right] \right\} - 1.$$
(26)

The multi-component population polynomial contains K (number of components) unknown monomer populations N_c . Thus, the central obstacle that hampered the development of a generalized QCE theory for multi-component systems so far, is the need for K - 1additional, linearly independent equations. To illustrate this, we start from a neat system of K = 1 component where eq. (26) is reduced to

$$0 = \sum_{i}^{L} \frac{n_i^a q_1}{\mathcal{N}_1^{\text{tot}}} \cdot \left(\frac{N_1}{q_1}\right)^{n_i^a} - 1, \qquad (27)$$

that can be solved for N_1 . Extending this to a binary system with K = 2 components, we obtain

$$0 = \sum_{i}^{L} \frac{n_{i}^{a} + n_{i}^{b}}{\mathcal{N}_{1}^{\text{tot}} + \mathcal{N}_{2}^{\text{tot}}} \cdot q_{i} \left(\frac{N_{1}}{q_{1}}\right)^{n_{i}^{a}} \left(\frac{N_{2}}{q_{2}}\right)^{n_{i}^{b}} - 1,$$
(28)

with the two unknown monomer populations N_1 and N_2 . The solution requires the introduction of a second linearly independent equation. In case of binary systems, this issue could be circumvented by introducing the mass polynomial as a second condition (see eq. (17)). Accordingly, more linearly independent equations are required for systems with more than two components. In general, the conservation of physical quantities is a possible but not the only approach to generate new and linearly independent equations. For ternary systems, one could think of introducing another conserved quantity, e.g. the total cluster volume. However, this idea is not seen as a viable option as it does not lead to a general solution for systems with more than three components.

Instead, the path to a generalized population polynomial (eq. (26)) leads through the realization that for binary systems, neither the exact values of m_1 and m_2 in eq. (17) nor their ratio changes the exact results of the population polynomial, as long as the total mass is conserved. Following this, eq. (17) can be generalized to conserve any quantity Z.

$$\sum_{c}^{K} Z_c \mathcal{N}_c^{\text{tot}} = \sum_{i}^{L} \sum_{c}^{K} n_i^c Z_c N_i$$
(29)

$$0 = \frac{1}{\sum_{c}^{K} Z_{c} \mathcal{N}_{c}^{\text{tot}}} \sum_{i}^{L} \sum_{c}^{K} \{ n_{i}^{c} Z_{c} \cdot N_{i} \} - 1.$$
(30)

In eq. (29), K linearly independent realizations of Z, referenced as Z_c , are introduced to create a set of K linearly independent equations. Each Z_c is a set of K coefficients that could be considered elements of a vector. From that, a new population polynomial can be formulated:

$$0 = \frac{1}{\sum_{c}^{K} Z_{c} \mathcal{N}_{c}^{\text{tot}}} \sum_{i}^{L} \sum_{c}^{K} \left\{ n_{i}^{c} Z_{c} \cdot \prod_{c} \left[q_{i} \left(\frac{N_{c}}{q_{c}} \right)^{n_{i}^{c}} \right] \right\} - 1.$$
(31)

 Z_c is explicitly not required to represent any physical quantity. Hence, the solution of eq. (31) is not restricted to the conservation of mass, volume, or any other physical quantity. More precisely, the solution is achieved by creating K linearly independent sets of coefficients.

Proof. We start from eq. (29) by rewriting it in a vectorized form:

$$\vec{Z}^T \vec{\mathcal{N}}^{\text{tot}} = \vec{Z}^T \mathbf{n} \vec{\mathcal{N}}.$$
(32)

In eq. (32), each of the K different Z_c is expressed as a K-dimensional vector \vec{Z} . Moreover, $\vec{\mathcal{N}}^{\text{tot}}$ is a vector with K entries containing the total number of monomers of the K components c, **n** is a $(K \times L)$ -matrix containing the coefficients n_i^c and \vec{N} is a L-dimensional vector containing the populations of the L different clusters. This can be rearranged to

$$\vec{Z}^T (\mathbf{n}\vec{N} - \vec{\mathcal{N}}^{\text{tot}}) = 0 \tag{33}$$

$$\Leftrightarrow \quad \vec{Z}^T \perp (\mathbf{n}\vec{N} - \vec{\mathcal{N}}^{\text{tot}}). \tag{34}$$

The above condition is only fulfilled for any vector \vec{Z} , if either $\vec{Z}^T = 0$ or $(\mathbf{n}\vec{N} - \vec{N}^{\text{tot}}) = 0$. The former condition does not lead to a meaningful solution and hence, is excluded. The latter leads to the condition

$$\mathbf{n}\vec{N} = \vec{\mathcal{N}}^{\text{tot}} \tag{35}$$

representing the conservation of particles.

Furthermore, it should be stated that for binary systems eq. (31) simplifies to eqs. (15) and (17) in the particular cases when Z_c is unity or contains m_1 and m_2 , respectively.

With these sets of coefficients at hand, a system of non-linear equations can be formulated and solved for the monomer populations N_c . This is done in a self-consistent manner, utilizing a generalized volume polynomial

$$0 = -pV^{3} + \left(\sum_{i}^{L} k_{\rm B}TN_{i} + pV_{\rm ex}\right)V^{2}$$
$$- \left(\sum_{i}^{L}\sum_{c}^{K} n_{i}^{c}N_{i}a_{\rm mf}\right)V$$
$$+ a_{\rm mf}\sum_{i}^{L}\left[\sum_{c}^{K} n_{i}^{c}N_{i}\right]V_{\rm ex}.$$
(36)

The polynomial is solved iteratively, together with the population polynomial as introduced before.

3 Computational details

Ternary mixtures of chloroform (c), methanol (m), and water (w) were investigated by means of the mQCE theory as implemented in PEACEMAKER 3.⁵¹ Compositions of clusters are characterized by $c_i m_j w_k$ where i, j, k denote the number of monomers of the respective species (c, m, or w) contained in a cluster. Clusters of all possible compositions that obey $i, j, k \in \mathbb{N}_0$, with $i + j + k \leq 6$ are realized. In total, 185 different clusters were used, including multiple clusters of the same composition. A selected subset of clusters is shown in fig. 1. It should be noted that the description of bulk properties may be limited by the maximum cluster size, as cooperativity effects may not be fully captured by small clusters. A previous QCE study demonstrated that the inclusion of cooperativity effects is necessary for a realistic description of liquid water,⁴⁶ but included no investigation of cluster size effects. In 2021, a study of nine aprotic organic liquids, including clusters up to the size of ten molecules, showed that a maximum cluster size of six molecules may be sufficient to obtain reasonable vaporization enthalpies.³⁸ However, a systematic QCE study of cluster size effects in coordinating liquids such as water is unavailable at the time of writing but may be subject to future investigations. The maximum cluster size of six molecules in the current study was chosen as it has led to reasonable results in previous works 38,52 and offers an acceptable balance between accuracy and computational effort. Figure S1 in the Supporting Information shows how the maximum cluster size of the cluster set affects the vaporization enthalpies of the neat compounds. For methanol $\Delta_{vap}H$ converges at a cluster size of six molecules. In the case of water, however, the inclusion of larger clusters leads to an overestimation of $\Delta_{vap}H$, demonstrating that the appropriate cluster size is dependent on the system. This is important especially in multi-component systems, as the cluster set should include a balanced representation of all possible cluster compositions within the chosen cluster size limit to avoid introducing a bias to either neat or mixed clusters. The current study therefore serves as an illustrative example of the extension to the QCE theory, but a detailed investigation of cooperativity and cluster size effects is essential for future



Figure 1: Selected subset of clusters to describe ternary mixtures of chloroform (c), methanol (m) and water (w). The color code of the molecules is: hydrogen (white), carbon (orange), oxygen (red), chlorine (green).

investigations.

The cluster set was created using the genetic algorithm OGOLEM, ^{53,54} interfaced with the AMBER 2016⁵⁵ molecular dynamics software package. For each composition, a structurally diverse set of molecular geometries was chosen and optimized at the GFN2-xTB⁵⁶ level of theory. For each cluster, harmonic frequencies were calculated to identify minimum structures. The final cluster set comprises clusters without imaginary frequencies, exclusively. The GFN2-xTB method was previously shown to produce reasonable results in combination with the bQCE method.^{38,52} Extensive comparisons of various quantum-chemical methods in combination with the QCE method can be found in literature, e.g. Ref. 41 and 57.

All mQCE calculations were performed at a constant pressure of 1.01325 bar and a temperature range of 273.15 to 400.15 K. Cluster volumes were calculated as van der Waals volumes with radii taken from the compilation of Bondi.⁵⁸ The parameters $a_{\rm mf}$ and $b_{\rm xv}$ were optimized for each pure component using its experimental density at 298.15 K and boiling point, as reported in Ref. 59. Initially, a rough 20 × 20 grid sampling between 0.0 to 2.0 J m³ mol⁻¹ and 0.5 to 1.5 for $a_{\rm mf}$ and $b_{\rm xv}$, respectively, was performed with uniformly distributed sampling points. Using the parameter pair with the lowest deviation from exper-



Figure 2: Vaporization enthalpies $\Delta_{vap}H$ of ternary mixtures of chloroform, methanol and water as a function of the mixture composition.

imental data as starting point, the Nelder–Mead algorithm was then employed to optimize $a_{\rm mf}$ and $b_{\rm xv}$ further until the computed properties reproduced the experimental reference with chemical accuracy. Following the same procedure as in previous works, ^{33,52} the parameters at all mixed compositions were calculated from linear interpolation. Additionally, in order to calculate enthalpies of vaporization $\Delta_{\rm vap}H$ at room temperature, parameter-free QCE⁰ calculations were performed as a gas phase reference. For QCE⁰ calculations the parameters are set to $a_{\rm mf} = 0 \,\mathrm{J}\,\mathrm{m}^3\,\mathrm{mol}^{-1}$ and $b_{\rm xv} = 1$, cancelling all inter-cluster interactions.

4 Case study

In this section, we present thermodynamic properties for the ternary mixtures of chloroform, methanol and water, as obtained from the mQCE method. Experimental thermodynamic data for ternary mixtures in a meaningful mole fraction range are rarely available. In consideration of the fact that the QCE theory has been successful in predicting thermodynamic properties of neat liquids and binary mixtures, we focus on the exemplary and illustrative case study of the vaporization enthalpy here and leave a more detailed comparison to experimental data for future works.

Whereas vaporization enthalpies of neat liquids are easily defined as the enthalpy difference between the liquid and the gas phase at any given temperature, in multi-component systems the difference in composition of the liquid phase presents a more complex situation. In the literature, usually, the integral enthalpy of vaporization is reported, corresponding to the transfer of a liquid mixture at its bubble temperature to a gaseous mixture of the same composition at its dew point. The computational mQCE approach allows the calculation of enthalpies of vaporization at standard conditions. Here, isobaric vaporization enthalpies $\Delta_{\rm vap}H$ were calculated according to:

$$\Delta_{\rm vap} H(\mathbf{x}_1, \mathbf{x}_2, T) = H_{\rm gas}(\mathbf{x}_1, \mathbf{x}_2, T) - H_{\rm l}(\mathbf{x}_1, \mathbf{x}_2, T), \tag{37}$$

where T = 298.15 K and the pressure was set to 1.01325 bar. Following the same procedure as in previous works, ^{35,52} H_1 is available as a result of the standard QCE procedure and the gas phase enthalpy H_{gas} was obtained from QCE⁰ calculations. The calculated vaporization enthalpies of the neat liquids are listed in table 1 next to their experimental reference values. Excellent agreement between the calculated and experimental values is observed for all three components, with deviations falling below 2.5 kJ mol⁻¹, well within the range of chemical accuracy.

The calculated vaporization enthalpies of the mixed systems are depicted as a function of the mole fractions x_c , x_m , and x_w in fig. 2. The triangle plot shows the same general trends as observed in the neat liquids, in that a higher water amount leads to a higher vaporization enthalpy. Remarkably, there is an exception to that behavior at low methanol concentrations, where a valley can be observed with a minimum around a composition of

Table 1: Experimental and calculated vaporization enthalpies $\Delta_{\text{vap}}H$ and differences $\Delta(\Delta_{\text{vap}}H)$ (all in kJ mol⁻¹) of chloroform, methanol and water in comparison to the mQCE results.

	Exp.	mQCE	$\Delta(\Delta_{\rm vap}H)$
chloroform	$\begin{array}{r} 31.32 \pm 0.08^{60} \\ 37.43 \pm 0.02^{61} \\ 43.87 \pm 0.03^{62} \end{array}$	28.95	-2.37
methanol		39.20	1.77
water		41.85	-2.02

 $x_c = 0.60$, $x_m = 0.00$, $x_w = 0.40$. This finding can be rationalized by the fact that water and chloroform are hardly miscible and form a minimum-boiling azeotrope at a mole fraction of $x_c = 0.84$.⁵⁹ Notably, this first application of the mQCE method leads to an explanation of an interesting thermodynamic phenomenon, observed in the mixing of a ternary mixture.

Additionally, fig. 3 shows the most populated clusters at each investigated composition of the ternary mixture. The corners of the triangular plot, corresponding to compositions close to the neat liquids, are dominated by larger aggregates of the pure components, namely the c_4 , m_5 , and w_6 clusters. On the other hand, in a large and central part of the molar range, the mixed c_1w_1 cluster is predominant. While surprising at first glance, this finding is indicative of the unfavorable mixed interactions of larger clusters formed between water and chloroform. Instead, the hydrogen bond network formed by larger aggregates of water and methanol molecules is disrupted in favor of smaller, enthalpically unfavorable clusters. This leads to a destabilization of the liquid phase, visible in the observed minimum in the vaporization enthalpy and also the immiscibility of water and chloroform.

5 Conclusions

In this paper, we provided a comprehensive and detailed description of the theory underlying the quantum cluster equilibrium method. For the first time since it was introduced, the theory was extended from binary liquids to multi-component systems, now being capable of describing mixtures with an arbitrary number of distinct chemical species. This enables



Figure 3: Highest populated cluster composition as a function of the mixture composition. Clusters with identical composition, but different conformation are represented in an accumulated manner.

studying important structural motifs and interactions in bulk phases of any composition by means of the QCE theory. The extension to multi-component systems was achieved by eliminating the need for conserved physical quantities, such as the cluster mass, from the system of equations used to solve the population polynomial. In the updated implementation, a generalized population polynomial is introduced, allowing for the solution with an arbitrary number of components. This is achieved through the utilization of a set of auxiliary parameters that do not depend on a direct physical relationship. A mathematical proof for the new formalism was included.

Finally, we presented an exemplary study of the vaporization enthalpy in the ternary mixture of chloroform, methanol and water. The experimental vaporization enthalpies of the neat components are precisely replicated within chemical accuracy. For the mixed system, the mQCE method predicts reasonable values that can easily be rationalized. The mQCE theory is implemented in our free and open-source software PEACEMAKER and available from Ref. 51.

Data availability

The data underlying this study are publicly available on our mQCE data repository.

Supporting Information Available

In order to present a complete and self-contained introduction to mQCE theory, the Supporting Information provide an overview of basic equations of thermochemistry. Additionally, the relationship between the QCE parameters and the van der Waals equation is established. Finally, we investigate how the maximum cluster size affects $\Delta_{vap}H$ in the neat liquids.

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TOC Graphic

