Supporting Information: A Quantum Cluster Equilibrium Theory for Multi-Component Liquids

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1 Basic equations from thermochemistry

The QCE theory is founded on basic equations from thermochemistry, derived from statistical mechanics. Therefore, important concepts are briefly recapitulated in the following. The thermodynamic ensemble the QCE theory is defined in, is the canonical ensemble (NVT), characterized by a constant number of particles N, volume V, and temperature T. The partition function of the canonical ensemble is denoted by Q (further referenced to as system partition function) and is given by a sum over the *Boltzmann* factors of all possible microstates j of the system with their energies E_j and the *Boltzmann* constant k_B:

$$Q = \sum_j \mathrm{e}^{-\frac{E_j}{k_\mathrm{B}T}}. \tag{1}$$

The probability p_j of the system being in microstate j is then given by

$$p_j = \frac{1}{Q}\mathrm{e}^{-\frac{E_j}{k_\mathrm{B}T}}, \tag{2}$$

while the sum of all probabilities equals unity. The partition function is the central quantity in statistical mechanics and the QCE theory, as all thermodynamic properties can be derived from it. For further reading on this, we refer to standard textbooks, such as Ref. S1. When treating a system of *indistinguishable* particles, the partition function can be written as

$$Q = \frac{1}{N!}\, q^N, \tag{3}$$

where q denotes the partition function of a single particle. The energy ε of a particle can be decomposed into independent contributions from different degrees of freedom, such as translation, rotation, vibration, and electronic excitations:

$$\varepsilon = \varepsilon^\mathrm{trans} + \varepsilon^\mathrm{rot} + \varepsilon^\mathrm{vib} + \varepsilon^\mathrm{elec}. \tag{4}$$

Hence, q can be written as a product of the partition functions of the different degrees of freedom:

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

The exact expressions for the partition functions are derived from the models of the particle in a box, the rigid rotator, and the harmonic oscillator:

$$q^{\text{trans}} = \frac{V}{\Lambda^3}, \qquad \Lambda = \sqrt{\frac{h^2}{2\pi m k_\text{B} T}}, \tag{6a}$$

$$q^{\text{rot}} = \frac{\pi^{1/2}}{\sigma}\sqrt{\frac{T^3}{\Theta_A^{\text{rot}}\Theta_B^{\text{rot}}\Theta_C^{\text{rot}}}}, \qquad \Theta^{\text{rot}} = \frac{h^2}{8\pi^2 I k_\text{B}}\ , \tag{6b}$$

$$q^{\text{vib}} = \prod_{l=1}^{3N-x} \frac{\mathrm{e}^{-\Theta_l^{\text{vib}}/2T}}{1-\mathrm{e}^{-\Theta_l^{\text{vib}}/T}}, \qquad \Theta_l^{\text{vib}} = \frac{h\nu_l}{k_\text{B}}. \tag{6c}$$

In the above equations, h is the *Planck* constant, m the particle mass, σ the rotational symmetry number, I the moment of inertia, $3N - x$ the number of vibrational degrees of freedom (with $x = 5$ for linear molecules and $x = 6$ else), and ν_l the vibrational frequency of the lth normal mode. The electronic partition function q^{elec} is given by the sum of the *Boltzmann* factors of the electronic states $\varepsilon^{\text{elec}}$, multiplied with the degeneracy g of the states. Usually, molecules are in the electronic ground state under ambient conditions, and hence, q^{elec} simplifies to

$$q^{\text{elec}} = g_1 \mathrm{e}^{-\frac{\varepsilon_1^{\text{elec}}}{k_\text{B}T}}. \tag{7}$$

2 mQCE and the van der Waals equation

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. This can be demonstrated by deriving an expression for the pressure based on the cluster partition functions. The total partition function of a system of molecular clusters is given by:

$$Q = \prod_{i}^{L} \frac{1}{N_i!}\, q_i^{N_i}. \tag{8}$$

We recall the connection between the system pressure and the total system partition function. By insertion of eq. (8), we obtain:

$$p = k_\mathrm{B}T\frac{\partial \ln Q}{\partial V} = \prod_i^L N_i k_\mathrm{B}T\frac{\partial \ln q}{\partial V}. \tag{9}$$

Of the partition functions in eq. (5), only q^trans and q^elec depend on the system's volume:

$$\begin{aligned}\frac{\partial \ln q_i}{\partial V} &= \frac{\partial \ln q_i^\mathrm{trans}}{\partial V} + \frac{\partial \ln q_i^\mathrm{elec}}{\partial V}\\ &= \frac{\partial\left(\ln(V - V_\mathrm{ex}) - 3\ln\Lambda\right)}{\partial V} + \partial\left(\frac{\Delta_\mathrm{bind}\varepsilon^\mathrm{elec} - \sum_c^K n_i^c\frac{a_\mathrm{mf}}{V}}{k_\mathrm{B}T}\right)\frac{1}{\partial V}\\ &= \frac{1}{V - V_\mathrm{ex}} - \sum_c^K n_i^c\frac{a_\mathrm{mf}}{k_\mathrm{B}TV^2}.\end{aligned} \tag{10}$$

By insertion into eq. (9) we obtain:

$$\begin{aligned}p =& \prod_i^L \frac{N_i k_\mathrm{B}T}{V - V_\mathrm{ex}} - \prod_i^L \frac{N_i\sum_c^K n_i^c a_\mathrm{mf}}{V^2}\\ =& \frac{\prod_i^L N_i k_\mathrm{B}T}{V - b_\mathrm{xv}\sum_i^L N_i v_i} - \frac{\prod_i^L N_i\sum_c^K n_i^c a_\mathrm{mf}}{V^2}.\end{aligned} \tag{11}$$

We consider a minimal cluster set containing only the monomer of a single component, i.e., $K = L = n = 1$. Equation (11) then reduces to:

$$p = \frac{Nk_\mathrm{B}T}{V - Nb_\mathrm{xv}v} - \frac{Na_\mathrm{mf}}{V^2}. \tag{12}$$

By comparison to the van der Waals equation

$$p = \frac{Nk_\mathrm{B}T}{V - Nb} - \frac{N^2a}{V^2} \tag{13}$$

it is apparent that for $K = L = n = 1$ there is a direct connection between the QCE parameters and the van der Waals equation through $a_\mathrm{mf} = aN$ and $b_\mathrm{xv} = b/v$. An mQCE system can therefore be understood as a multi-component van der Waals fluid.

3 Cluster size effects

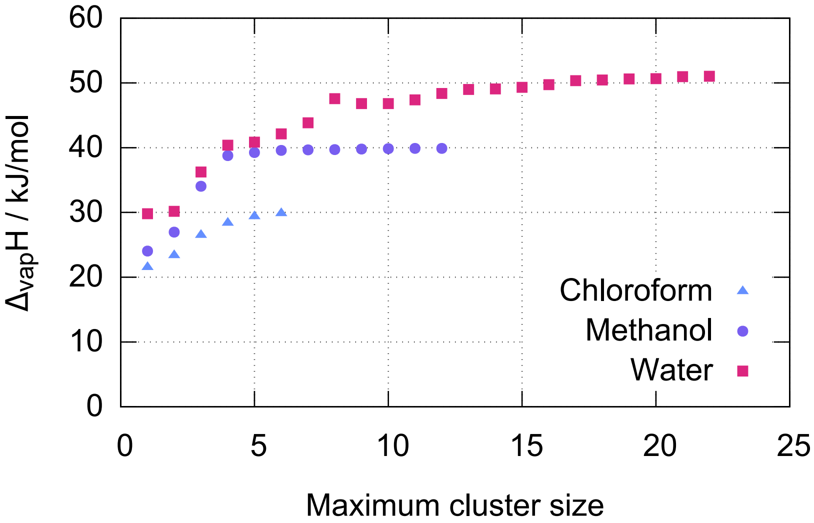

Figure S1: Enthalpy of vaporization $\Delta_{\mathrm{vap}}H$ for different pure compounds at 298.15 K and 1.013 25 bar as calculated from QCE depending on the maximum cluster size included in the cluster set.

In fig. S1, we show the dependence of the vaporization enthalpy $\Delta_{\mathrm{vap}}H$ of the pure compounds chloroform, methanol, and water, as a function of the maximum cluster size,

References

(S1) McQuarrie, D. A. *Statistical Mechanics*, 2000th ed.; University Science Books: Sausalito, Calif. Great Britain, 2000.