

Chapter 2

From Atomistic Calculations to Thermodynamic Quantities

This chapter gives a short summary of well-established as well as more recent pathways for extracting information about thermodynamic equilibrium quantities out of microscopic calculations, which are based on different approximations of quantum mechanics and as such only provide information about mechanical properties at first. The standard rigid rotor harmonic oscillator (rrho) model for the prediction of thermodynamic gas phase properties out of molecular quantities as well as its basis, the factorization of the N -particle partition function, will be revisited in detail along with a brief inspection of the different approximations this approach relies on. The quantum cluster equilibrium (qce) model will be exposed subsequently in terms of a van der Waals-like extension of the rrho approach for the thermodynamic treatment of condensed phases. In addition, several methods for computing thermodynamic equilibrium properties from molecular dynamics (md) simulations will be covered as well.

2.1 The Rigid Rotor Harmonic Oscillator Model

2.1.1 Essentials

2.1.1.1 The Classical N -Particle Partition Function

When dealing with the calculation of thermodynamic quantities from the fundamental molecular interactions, the ideas and methodologies of statistical thermodynamics are essential. The central quantity in statistical equilibrium thermodynamics is the partition function Q , which for a classical system of N identical and indistinguishable particles of mass m at temperature T confined to a volume V is given as [1]

$$Q_{\text{class}} = \frac{1}{N!h^{3N}} \int \exp(-\beta \mathcal{H}(\mathbf{p}, \mathbf{q})) d\mathbf{p} d\mathbf{q}. \quad (2.1)$$

In Eq. 2.1, β denotes the inverse temperature ($\beta = (k_B T)^{-1}$) and $\mathbf{q}, \mathbf{p}$ are vectors containing generalized coordinates and the corresponding conjugate momenta, respectively, of all particles in the system (i.e., in the case of Cartesian coordinates $d\mathbf{p} = dp_{1x} dp_{1y} dp_{1z} \dots dp_{Nx} dp_{Ny} dp_{Nz}$ and $d\mathbf{q} = dx_1 dy_1 dz_1 \dots dx_N dy_N dz_N$). The factor $N!^{-1}$ accounts for the redundancy of microstates introduced by the indistinguishability of the particles (for a detailed explanation see the part about the quantum mechanical limit in the following). In order to make the partition function dimensionless h has to be a normalization of the dimension momentum times length, which is taken to be the Planck constant, thereby ensuring consistency with the quantum mechanical limit [2, 3].

The Hamilton function represents the total energy of the system under examination and consists of a kinetic contribution $\mathcal{K}(\mathbf{p}) = \frac{1}{2m} \sum_{i=1}^N (p_{i,x}^2 + p_{i,y}^2 + p_{i,z}^2)$ and a configurational part $U(\mathbf{q})$ ¹

$$\mathcal{H}(\mathbf{p}, \mathbf{q}) = \mathcal{K}(\mathbf{p}) + U(\mathbf{q}). \quad (2.2)$$

The presumably most simple many-particle system is realized by a system consisting of non-interacting particles, i.e., an ideal gas. In this case $U(\mathbf{q}) = 0$, and due to the independence of the momenta of different particles the integral in Eq. 2.1 can be evaluated directly, yielding [1]

$$\begin{aligned} Q_{\text{class,ideal}} &= \frac{1}{N!h^{3N}} \int \exp(-\beta \mathcal{K}(\mathbf{p})) d\mathbf{p} d\mathbf{q} \\ &= \frac{1}{N!h^{3N}} \int \exp\left(-\frac{\beta}{2m} \sum_{i=1}^N p_{i,x}^2 + p_{i,y}^2 + p_{i,z}^2\right) dp_{1x} \dots dp_{Nz} dx_1 \dots dz_N \\ &= \left(\frac{2\pi m k_B T}{h^2}\right)^{3N/2} \frac{V^N}{N!}. \end{aligned} \quad (2.3)$$

In Eq. 2.3 each particle contributes three Gaussian-type integrals via its three momentum coordinates, and each of the N integrations over the spatial coordinates yields the volume of the container V .

The form of Eq. 2.3 suggests the possibility to decompose the N -particle partition function (Eq. 2.1) into contributions q from the single particles which constitute the N -particle system according to

¹ Please note that the system consists of identical particles, which is the reason for the uniform mass m occurring in the kinetic contribution.

$$Q_{\text{class,ideal}} = \frac{q^N}{N!}, \quad \text{where } q = \left(\frac{2\pi m k_B T}{h^2} \right)^{3/2} V. \quad (2.4)$$

Strictly speaking, Eqs. 2.3 and 2.4 are only valid in the absence of any interparticle interactions, but even in the case $U(\mathbf{q}) \neq 0$, the spatial and momentum coordinates are independent and a separation of the form

$$Q_{\text{class}} = \frac{1}{N!} \left(\frac{2\pi m k_B T}{h^2} \right)^{3N/2} \times Z, \\ \text{where } Z = \int \exp(-\beta U(x_1, \dots, z_N)) dx_1 \dots dz_N, \quad (2.5)$$

is possible. In this equation, Z is called the *configurational integral* of the system, which depends only on the interparticle interactions. However, it is because of Z that the partition function of an N -particle system in most cases cannot be evaluated analytically, since a decoupling of the coordinates in $U(\mathbf{q})$ is normally impossible.

The separability of the N -particle partition function in single particle contributions in the absence of interparticle interactions is a quite general result and constitutes the basis for the rrho approach.

2.1.1.2 The Quantum Mechanical Limit

The quantum mechanical analogon to the classical Hamilton function $\mathcal{H}$ is given by the Hamilton operator, which for an N -particle system of identical particles takes the form [1]

$$\hat{H} = \hat{K} + U = -\frac{\hbar^2}{2m} \sum_{i=1}^N \nabla_i^2 + U(x_1, \dots, z_N) \quad (2.6)$$

If $\{|\Psi_j\rangle\}$ denotes a set of eigenfunctions of $\hat{H}$, the Hamilton operator satisfies the Schrödinger equation

$$\hat{H}|\Psi_j\rangle = E_j|\Psi_j\rangle, \quad (2.7)$$

where E_j denotes the energy eigenvalue corresponding to the state the eigenfunction $|\Psi_j\rangle$ describes. Carrying out a one-to-one substitution according to Eq. 2.1 results in an expression of the form $\exp(-\beta\hat{H})$, which can be understood as a function of an operator. The effect of $\exp(-\beta\hat{H})$ on an eigenfunction of $\hat{H}$ can be illustrated by employing the corresponding MacLaurin expansion [1]

$$\begin{aligned} \exp(-\beta\hat{H})|\Psi_j\rangle &= \left(\sum_{n=0}^{\infty} \frac{(-\beta)^n}{n!} \hat{H}^n \right) |\Psi_j\rangle = \sum_{n=0}^{\infty} \frac{(-\beta)^n}{n!} \hat{H}^n |\Psi_j\rangle \\ &= \sum_{n=0}^{\infty} \frac{(-\beta)^n}{n!} E_j^n \Psi_j = \exp(-\beta E_j) |\Psi_j\rangle, \end{aligned} \quad (2.8)$$

which is again an eigenvalue equation. Solving for the j th eigenvalue, one obtains

$$\exp(-\beta E_j) = \langle \Psi_j | \exp(-\beta\hat{H}) | \Psi_j \rangle, \quad (2.9)$$

since $\hat{H}$ is a hermitian operator and the $\{|\Psi_j\rangle\}$ can be normalized to an orthonormal set.

After transferring the integrand of the classical N -particle partition function, one has to take care of the integration itself, since the states of a quantum mechanical system are not continuously distributed over its state space. The classical partition function in Eq. 2.1 can be understood as a volume integral over the exponentially weighted energies the N -particle system can adopt. However, according to Eq. 2.7 a quantum mechanical N -particle system has a discrete set of energy values and there is no way to populate the state space between these allowed states, which is the reason why the integration in Eq. 2.1 can be replaced by a corresponding sum over the allowed states according to

$$Q_{\text{qm}} = \sum_j \exp(-\beta E_j) = \sum_j \langle \Psi_j | \exp(-\beta\hat{H}) | \Psi_j \rangle = \text{tr}([\exp(-\beta\hat{H})]). \quad (2.10)$$

Since the trace of a linear operator's matrix representation is independent of the basis, the set $\{|\Psi_j\rangle\}$ is not particular in any form and Eq. 2.10 is a most general result as in case of Eq. 2.1, where in analogy the generalized coordinates $\mathbf{q}$, $\mathbf{p}$ are not restricted to any special set [1].

According to Eq. 2.10, it is possible to calculate the partition function of a quantum mechanical N -particle system if either its energy eigenvalues or a basis of its state space is known. Despite this fact, Eq. 2.10 is of little practical use, since the Schrödinger equation Eq. 2.7 is exactly solvable only for one- and two-particle problems, and feasible approximations can be applied to systems of hundreds or thousands particles, which is far from the order of magnitude of macroscopic particle numbers ($\sim 10^{23}$) [4]. As in the classical case, a pragmatic approach to this size problem can be obtained by looking at an N -particle system without inter-particle interactions (i.e., an ideal quantum gas), since it is clear from Eq. 2.6 that the coupling between the particles is again solely due to the interaction potential $U(x_1, \dots, z_N)$. Setting $U(x_1, \dots, z_N) = 0$, the many-body Hamilton operator $\hat{H}$ can be decomposed into a sum of single particle contributions $\hat{h}_i$ [5]

$$\hat{H} = \sum_{i=1}^N \hat{h}_i, \quad \text{where } \hat{h}_i = -\frac{\hbar^2}{2m} \nabla_i^2. \quad (2.11)$$

Ignoring any possible symmetry constraints like the Pauli principle, the decoupling of the many-body Schrödinger equation Eq. 2.7 into single particle equations for this case can be realized via a wave function product ansatz of the form $|\Psi_j\rangle = |\psi_{j,1}\dots\psi_{j,i}\dots\psi_{j,N}\rangle$, where the set $\{\psi_{j,i}\}$ contains single particle eigenfunctions of the operators $\hat{h}_i$. The single particle Schrödinger equations thus take the form

$$\hat{h}|\psi_k\rangle = \epsilon_k|\psi_k\rangle, \quad (2.12)$$

where k labels the energy states of the single particle system. In this setup, every energy state E_j of the macrosystem can be expressed as a sum of the single particle energies $\{\epsilon_k\}$

$$E_j = \left(\epsilon_{k(1)}^{(1)} + \epsilon_{k(2)}^{(2)} + \dots + \epsilon_{k(N)}^{(N)} \right) = \sum_{i=1}^N \epsilon_{k(i)}^{(i)}. \quad (2.13)$$

Each of the N identical particles will be in one of the single particle states labeled by k , i.e., the energy state can be understood as a function of the particle number, which is indicated by the label $k(i)$. Although all energy states E_j of the N -particle system can be written as sums of the single particle energies $\epsilon_{k(i)}^{(i)}$, this expansion is not unique in the case of identical particles, since a permutation of two or more indices will not change the resulting macrostate E_j . Consider for instance the expansions $\epsilon_1^{(1)} + \dots + \epsilon_3^{(m)} + \epsilon_4^{(n)} + \dots$, in which particle m is in energy state 3 and particle n is in energy state 4, and $\epsilon_1^{(1)} + \dots + \epsilon_4^{(m)} + \epsilon_3^{(n)} + \dots$, in which particle m is in energy state 4 and particle n is in energy state 3. Both sums finally lead to the same N -particle state E_j and therefore only one of them has to be included in an enumeration of the macrostates. For that reason it is more appropriate to assign occupation numbers $\{n_k\}$ to the single particle states $\{\epsilon_k\}$ in a system of identical particles and express the N -particle state according to [6]

$$E_j = \sum_k n_k \epsilon_k. \quad (2.14)$$

The values of n_k directly correspond to the number of particles occupying state ϵ_k , and the summation is now carried out over the single particle states labeled by k and no longer over the particles as in Eq. 2.13. Before evaluating the N -particle partition function in Eq. 2.10 with the aid of Eq. 2.14, one has to consider the correct weight for each of the macrostates E_j . As illustrated in the example above, it does not matter which of the individual particles occupies a given single particle state in a system of identical particles. This is the reason why a given macrostate E_j is completely characterized by the set of occupation numbers $\{n_k\}$. The correct weight g_j for the state E_j is thus given as

$$g_j(\{n_k\}) = \frac{N!}{n_1!n_2!\dots} = \frac{N!}{\prod_k n_k!}, \quad (2.15)$$

which represents the number of possibilities to distribute the N identical particles with respect to the particular values of the occupation numbers $\{n_k\}$ constituting E_j according to Eq. 2.14 [7]. Applying these ideas, the N -particle partition function can be factorized in the following way (see also Sect. 7.2 in Chap. 7)

$$\begin{aligned} Q_{\text{qm,ideal}} &= \sum_j g_j \exp(-\beta E_j) = \sum_{\{n_k\}} \frac{N!}{\prod_k n_k!} \exp\left(-\beta \sum_k n_k \epsilon_k\right) \\ &= \sum_{\{n_k\}} \frac{N!}{\prod_k n_k!} \prod_k \exp(-\beta n_k \epsilon_k) \\ &= N! \sum_{\{n_k\}} \prod_k \frac{[\exp(-\beta \epsilon_k)]^{n_k}}{n_k!}, \end{aligned} \quad (2.16)$$

where $\sum_{\{n_k\}}$ indicates the summation over all possible combinations of the occupation numbers n_k consistent with the condition $N = \sum_k n_k$. Equation 2.16 already represents a factorization into single particle contributions, but in general the summation over the sets of occupation numbers and the product over the energy states k cannot be exchanged as in case of the integration for a classical system, see Eq. 2.3.² In order to proceed further, a mathematical theorem known as the multinomial theorem has to be applied, which is given by [1, 7]

$$(x_1 + x_2 + \dots + x_m)^c = \sum_{\alpha_1, \alpha_2, \dots, \alpha_m} \left(\frac{c!}{\alpha_1! \alpha_2! \dots \alpha_m!} \right) x_1^{\alpha_1} x_2^{\alpha_2} \dots x_m^{\alpha_m}. \quad (2.17)$$

As in Eq. 2.16, the summation over the set $\{\alpha_k\}$ is restricted according to $\sum_k \alpha_k = c$, and $x_1, x_2, \dots$ can be identified with the exponentials from Eq. 2.16. Comparing Eqs. 2.17 and 2.16, the final factorization is obtained as

$$\begin{aligned} Q_{\text{qm,ideal}} &= \sum_{\{n_k\}} \prod_k \frac{N!}{n_k!} [\exp(-\beta \epsilon_k)]^{n_k} \\ &= [\exp(-\beta \epsilon_1) + \exp(-\beta \epsilon_2) + \dots]^N \\ &= \left[\sum_k \exp(-\beta \epsilon_k) \right]^N \\ &= q^N, \quad \text{where } q = \sum_k \exp(-\beta \epsilon_k). \end{aligned} \quad (2.18)$$

Equation 2.18 demonstrates that one can calculate the partition function of a non-interacting N -particle system composed of identical particles from the single

² In fact, Eq. 2.16 does not represent any real simplification, because if the occupation numbers $\{n_k\}$ would be known for a macroscopic system, the N -particle state energies could be computed according to Eq. 2.14 and the N -particle partition function could be calculated in the conventional way, see Eq. 2.10.

particle partition functions q and the total number of particles N , thereby representing a real size reduction from the N -particle macrosystem to the single particle scale. However, by applying the weighting factor for the macrostates E_j from Eq. 2.15 one important restriction is tacitly assumed, namely the distinguishability of the N identical particles. If the N particles in turn are taken to be indistinguishable, there are no longer $N!$ different arrangements which could be distinguished from each other, but only one single arrangement. Therefore the transition from distinguishable to indistinguishable particles is formally achieved by a division by $N!$ as in the classical case, compare Eq. 2.3. The correct weight g_j of a given macrostate E_j for this case is thus given as [7]

$$g_j(\{n_k\}) = \frac{1}{n_1!n_2!\dots} = \frac{1}{\prod_k n_k!}, \quad (2.19)$$

and the factorization of the N -particle partition function can be expressed as

$$\begin{aligned} Q_{\text{qm,ideal}} &= \sum_{\{n_k\}} \prod_k \frac{1}{n_k!} [\exp(-\beta\epsilon_k)]^{n_k} \\ &= \frac{1}{N!} \left[\sum_k \exp(-\beta\epsilon_k) \right]^N \\ &= \frac{q^N}{N!}, \end{aligned} \quad (2.20)$$

where the single particle partition function q has the same meaning as in Eq. 2.18. An identical reduction was obtained for the classical setup (see Eq. 2.4), and factorization approaches of this kind constitute the first step towards the link between macroscopic thermodynamic state functions and atomistic calculations. However, up to this point Eqs. 2.18 and 2.20 are still of limited practical use, since in general there is an unlimited number of single particle states $\{\epsilon_k\}$ and the evaluation of the single particle partition functions q is not straightforward. In order to obtain a working relation for the computation of the N -particle partition function, approximations have to be introduced. Furthermore, in the treatment of chemically relevant systems one has to consider internal degrees of freedom for the particles as well as possible symmetry constraints on the N -particle wave function $|\Psi_j\rangle$, which have been omitted from the derivation up to now.

2.1.2 Molecular Systems and Approximations

2.1.2.1 Factorization of the Single Particle Partition Function

The conception presented in the last two parts emphasizes the formal difference between distinguishable and indistinguishable particles, but does not consider their

internal structure. Even the simplest atomic systems will exhibit translational and electronic degrees of freedom, and in the case of molecular systems there will be rotational and vibrational contributions as well. The results of the last section show that in order to obtain the partition function Q for a non-interacting N -particle quantum system composed of indistinguishable and identical particles, it is sufficient to compute the single particle partition function q

$$q = \sum_k \exp(-\beta \epsilon_k), \quad (2.21)$$

where the phrase “particle” now stands for a single atom or even a molecule (i.e., a collection of elementary particles). The molecular energy states $\{\epsilon_k\}$ are solutions to the M -nuclei, n -electron Schrödinger equation, which, however, is not exactly solvable in general. Even if these solutions were available, there would be an unlimited number of them and the summation in Eq. 2.21 not necessarily has to converge to a well-defined limit. In order to tackle the problem, a series of approximations is usually applied, which, taken together, constitute the so-called rigid rotor harmonic oscillator approach [1]. The first of these approximations is the well-known Born-Oppenheimer approximation, which separates the molecular Schrödinger equation into two simpler equations, one for the electronic degrees of freedom (treating the nuclei as a constant external field) and one for the nuclear degrees of freedom (treating the electrons as a collective averaged potential) [5]. The Born-Oppenheimer approximation thus decouples the nuclear motion from the electronic motion, and the molecular Hamilton operator can be written as [8, 9]

$$\hat{h} = \hat{h}_{\text{el}} + \hat{h}_{\text{nuc}}, \quad (2.22)$$

where the electronic Hamilton operator $\hat{h}_{\text{el}}$ includes the electron-nuclei interaction for a set of fixed positions of the nuclei and the nuclear Hamilton operator $\hat{h}_{\text{nuc}}$ governs the motion of the nuclei.

The effect of an additive decomposition of the Hamilton operator as in Eq. 2.22 was already examined in the last section, compare Eqs. 2.11 and 2.13. For these equations it has been shown that the partition function of composite systems can be written as the product of the component partition functions if the Hamilton operator for the composite system is given as the sum over the Hamilton operators for each component, see Eq. 2.18. This general result can directly be applied to Eq. 2.22, which for the molecular partition function q yields a factorization of the form

$$q = q_{\text{nuc}} q_{\text{el}}. \quad (2.23)$$

Ignoring excited states of the nuclei (which are not populated in significant fractions at terrestrial temperatures), the remaining molecular degrees of freedom besides the electronic excitations arise from the translational motion of the whole molecule as well as rotations and vibrations. If there are no external fields present,

the contributions entering the molecular Hamilton operator only depend on the relative distance between the nuclei [5]. In this case, the translational motion can always be separated from the other degrees of freedom by considering the translational motion of the center of mass and treating the internal degrees of freedom in a center of momentum frame, in which the molecular center of mass is at rest and only the relative motion of the nuclei is accounted for [1]. Since these motions are uncoupled, the nuclear Hamilton operator further reduces to

$$\hat{h}_{\text{nuc}} = \hat{h}_{\text{trans}} + \hat{h}_{\text{int}}, \quad (2.24)$$

where $\hat{h}_{\text{trans}}$ represents the Hamilton operator for the center of mass translation and $\hat{h}_{\text{int}}$ accounts for the remaining internal degrees of freedom, i.e., rotations and vibrations. The final decoupling of rotational ($\hat{h}_{\text{rot}}$) and vibrational ($\hat{h}_{\text{vib}}$) motion is rationalized on the basis of different timescales for these degrees of freedom as well as the observation that the vibrational amplitudes in many cases are small compared to the equilibrium distances between the nuclei, which justifies the treatment of rotations as being rigid [1, 10]. Following this reasoning, the nuclear Hamilton operator is given according to

$$\hat{h}_{\text{nuc}} = \hat{h}_{\text{trans}} + \hat{h}_{\text{int}} = \hat{h}_{\text{trans}} + \hat{h}_{\text{rot}} + \hat{h}_{\text{vib}}. \quad (2.25)$$

The final equations underlying the rigid rotor harmonic oscillator approximation for a quantum system composed of N identical and indistinguishable molecules can thus be summarized as [1]

$$\begin{aligned} \hat{h} &= \hat{h}_{\text{el}} + \hat{h}_{\text{trans}} + \hat{h}_{\text{rot}} + \hat{h}_{\text{vib}}; \quad \epsilon_{k(w,l,J,v)} = \epsilon_{w,\text{el}} + \epsilon_{l,\text{trans}} + \epsilon_{J,\text{rot}} + \epsilon_{v,\text{vib}}; \\ q &= q_{\text{el}} q_{\text{trans}} q_{\text{rot}} q_{\text{vib}} \\ &= \left[\sum_w \exp(-\beta \epsilon_{w,\text{el}}) \right] \left[\sum_l \exp(-\beta \epsilon_{l,\text{trans}}) \right] \\ &\quad \times \left[\sum_J \exp(-\beta \epsilon_{J,\text{rot}}) \right] \left[\sum_v \exp(-\beta \epsilon_{v,\text{vib}}) \right]; \\ Q &= \frac{[q_{\text{el}} q_{\text{trans}} q_{\text{rot}} q_{\text{vib}}]^N}{N!}, \end{aligned} \quad (2.26)$$

where the notation $\epsilon_{k(w,l,J,v)}$ again indicates the dependency of the molecular state ϵ_k on the electronic state w , the translational state l , the rotational state J , and the vibrational state v . The set of approximations discussed above constitutes the main frame of the rigid rotor harmonic oscillator approach, but additional approximations will be necessary for the evaluation of the partition functions of the different degrees of freedom. These will be introduced in the following.

2.1.2.2 Translational Partition Function

According to Eq. 2.26 the translational contribution to the molecular partition function q takes the form

$$q_{\text{trans}} = \sum_l \exp(-\beta \epsilon_{l,\text{trans}}). \quad (2.27)$$

In order to evaluate this expression, an analytical form for the translational energy states $\{\epsilon_l\}$ has to be found. In the frame of the rrho approach, this is usually accomplished by treating the center of mass translation as the translation of a particle in a potential-free cubic box of length a with infinite potential walls at the borders of the box. This problem is a well-investigated quantum mechanical model system for which the analytic energy states are given as [11]

$$\epsilon(l_x, l_y, l_z) = \frac{h^2}{8ma^2} (l_x^2 + l_y^2 + l_z^2), \quad l_x, l_y, l_z \in \mathbb{N}^*, \quad (2.28)$$

where $\mathbb{N}^*$ denotes the natural numbers not including zero and m indicates the mass of the particle. The combination of Eqs. 2.27 and 2.28 results in

$$\begin{aligned} q_{\text{trans}}(V, T) &= \sum_{l_x, l_y, l_z}^{\infty} \exp(-\beta \epsilon(l_x, l_y, l_z)) = \sum_{l_x, l_y, l_z}^{\infty} \exp\left[-\frac{\beta h^2}{8ma^2} (l_x^2 + l_y^2 + l_z^2)\right] \\ &= \left[\sum_{l_x}^{\infty} \exp\left(-\frac{\beta h^2 l_x^2}{8ma^2}\right) \right] \left[\sum_{l_y}^{\infty} \exp\left(-\frac{\beta h^2 l_y^2}{8ma^2}\right) \right] \left[\sum_{l_z}^{\infty} \exp\left(-\frac{\beta h^2 l_z^2}{8ma^2}\right) \right] \\ &= \left[\sum_l^{\infty} \exp\left(-\frac{\beta h^2 l^2}{8ma^2}\right) \right]^3, \end{aligned} \quad (2.29)$$

where the last identity is valid due to the independence of the quantum numbers $\{l_k\}$ from each other. The sum occurring in the last line of Eq. 2.29 cannot generally be written in a closed form, which prevents a direct evaluation of q_{trans} . In order to obtain a working relation, an approximate treatment of the summation as an integration is normally done. This can be rationalized according to the following reasoning. The distance $\Delta \epsilon_l$ between adjacent translational states in most cases is very small compared to the thermal energy $k_B T$ at ambient temperatures. In these cases and at elevated temperatures, the discrete translational spectrum can thus be treated as a continuum, and therefore this approximation is referred to as the high temperature limit [11]. The same reasoning will again be employed in the discussion of the rotational partition function and in the consideration of symmetry constraints, see below. The application of that approximation results in a Gaussian-type integral, which can directly be evaluated according to

$$q_{\text{trans}} \approx \left(\int_0^\infty \exp \left[-\frac{\beta h^2 l^2}{8ma^2} \right] dl \right)^3 = \left(\frac{2\pi mk_B T}{h^2} \right)^{3/2} V, \quad (2.30)$$

where the volume V of the box is given as $V = a^3$. The result in Eq. 2.30 has already appeared before, namely as the single particle partition function in the classical treatment of an N -particle system of non-interacting particles, see Eq. 2.4. This is a plausible result, since the only single particle degrees of freedom in a system of non-interacting particles with no internal structure are expected to be translational degrees of freedom. It can also be seen that the ad hoc introduction of the Planck constant h in Eqs. 2.1 and 2.4 occurs in a natural way by treating translation as a quantum mechanical phenomenon in terms of the energy eigenvalues in Eq. 2.28.

A common practice in statistical thermodynamics is the introduction of the thermal de Broglie wavelength according to the following definition [1]

$$\Lambda = \left(\frac{h^2}{2\pi mk_B T} \right)^{1/2}. \quad (2.31)$$

Λ has units of length, and according to the classical equipartition theorem the average kinetic energy is given as $\langle \epsilon_{\text{kin}} \rangle = p^2/(2m) = (3/2)k_B T$, i.e., the average momentum equals $(mk_B T)^{1/2}$. Inserting this average momentum in the conventional de Broglie relation $\lambda = h/p$ indicates the analogy to the definition of Eq. 2.31, and accordingly the translational partition function can be written as

$$q_{\text{trans}} \approx \frac{V}{\Lambda^3}. \quad (2.32)$$

The thermal de Broglie wavelength Λ can be used to estimate the importance of quantum effects and the applicability of classical approximations like the high temperature limit, i.e., a classical or semi-classical treatment is only reasonable if $\Lambda^3/V \ll 1$ [11].

2.1.2.3 Rotational Partition Function

In order to obtain expressions for the molecular rotational energy states, the quantum mechanical model system of a rigid rotor is employed. The energy eigenvalues for this problem are given by [1]

$$\epsilon_J = \frac{\hbar^2 J(J+1)}{2I}, \quad J \in \mathbb{N}, \quad (2.33)$$

where I indicates the molecular moment of inertia and J denotes the rotational quantum number. Equation 2.33 is only valid in this form if the three principal moments of inertia I_A , I_B , I_C of the molecule under study are identical, i.e., if the

molecule belongs to the class of spherical tops [1]. The most general case of an asymmetric top ($I_A \neq I_B \neq I_C$) is a complicated problem and will not be treated in full detail here, but the quantum mechanical result for a spherical top can easily be generalized to the classical result for an asymmetric top in a plausible way. It is important to note that each of the energy states ε_J is degenerated by a factor $(2J + 1)^2$, which leads to the following form of the rotational partition function [1]

$$q_{\text{rot}}(T) = \sum_{J=0}^{\infty} (2J + 1)^2 \exp\left(-\beta \frac{\hbar^2 J(J + 1)}{2I}\right). \quad (2.34)$$

As in the case of the translational partition function, this sum cannot be expressed in any closed form, which is the reason why the summation again has to be approximated by an integration. The same reasoning leading to the high temperature limit in the case of the translational degrees of freedom can be applied for the rotational degrees of freedom as well, with possible exceptions to that given by molecular species showing small principal moments of inertia, for instance hydrogen. In this continuum limit, the rotational partition function can thus be written as [1]

$$\begin{aligned} q_{\text{rot}}(T) &\approx \int_0^{\infty} (2J + 1)^2 \exp\left(-\beta \frac{\hbar^2 J(J + 1)}{2I}\right) dJ \approx \int_0^{\infty} 4J^2 \exp\left(-\beta \frac{\hbar^2 J^2}{2I}\right) dJ \\ &\approx \pi^{1/2} \left(\frac{2Ik_{\text{B}}T}{\hbar^2}\right)^{3/2}, \end{aligned} \quad (2.35)$$

where in addition the increased importance of large values of J at high temperatures is assumed, so that $J^2 \gg J \gg 1$.

The rotational symmetry has another important impact on q_{rot} besides the classification as asymmetric or spherical top, namely in the case of the true number of distinguishable rotational states. If there are any rotational symmetry elements in the molecular point group which transfer the molecule into itself (besides a C_1 axis), there will be an overcounting of identical rotational states. As in the case of $g(\{n_k\})$ (see Eq. 2.15), the correct weighting can be obtained by neglecting the redundant states, which is formally achieved in terms of the symmetry number σ . In the general case of a polyatomic molecule, this number equals the order of the rotational subgroup of the molecular point group, i.e., $\sigma = 2$ for water and $\sigma = 12$ for benzene. A more elaborate derivation of the symmetry number on the basis of the molecular wave function can be found in [1] (see also the section about symmetry constraints). The consideration of this symmetry effect results in the following general form of the rigid rotor (rr) partition function

$$q_{\text{rr}}(T) = \frac{\pi^{1/2}}{\sigma} \left(\frac{2Ik_{\text{B}}T}{\hbar^2}\right)^{3/2}. \quad (2.36)$$

The generalization of Eq. 2.36 to asymmetric top structures can be achieved by inserting the classical Hamilton function of a rigid rotor into the classical partition function (see Eq. 2.1) and carrying out the integration. The result is given as [1]

$$\begin{aligned} q_{\text{r}}(T) &= \frac{\pi^{1/2}}{\sigma} \left(\frac{2I_a k_{\text{B}} T}{\hbar^2} \right)^{1/2} \left(\frac{2I_b k_{\text{B}} T}{\hbar^2} \right)^{1/2} \left(\frac{2I_c k_{\text{B}} T}{\hbar^2} \right)^{1/2} \\ &= \frac{\pi^{1/2}}{\sigma} \left(\frac{T^3}{\Theta_a \Theta_b \Theta_c} \right)^{1/2}, \end{aligned} \quad (2.37)$$

where $\Theta_{(a,b,c)}$ denotes the rotational temperature associated with the principal moments of inertia I_a , I_b , I_c according to

$$\Theta_{(a,b,c)} = \frac{\hbar^2}{2I_{(a,b,c)} k_{\text{B}}}. \quad (2.38)$$

It is apparent that this result reduces to the correct expression for a spherical top in the limit $I_a = I_b = I_c$.

Equation 2.37 represents a compact form of the rotational partition function and can be easily computed if the three principal moments of inertia are known. The central approximations employed in the derivation of Eq. 2.37 include the high temperature limit (Eq. 2.35) and the evaluation of the classical expressions in the case of asymmetric top structures.

2.1.2.4 Vibrational Partition Function

The quantum mechanical model system applied for the treatment of the molecular vibrational degrees of freedom is the model of the harmonic oscillator, for which the energy eigenvalues are given by [1]

$$\epsilon_v = \left(v + \frac{1}{2} \right) h\nu, \quad v \in \mathbb{N}. \quad (2.39)$$

Here ν denotes the oscillator's frequency, and for the case $\nu = 0$ the characteristic zero point energy $\epsilon_0 = \frac{h\nu}{2}$ of the oscillator is apparent from Eq. 2.39. According to Eqs. 2.26 and 2.39, the harmonic oscillator (ho) partition function q_{ho} can be expressed as

$$\begin{aligned} q_{\text{ho}}(T) &= \sum_{v=0}^{\infty} \exp \left(-\beta \left[v + \frac{1}{2} \right] h\nu \right) \\ &= \exp \left(-\frac{\beta h\nu}{2} \right) \sum_{v=0}^{\infty} \exp(-\beta v h\nu) \\ &= \frac{\exp(-\frac{1}{2} \beta h\nu)}{1 - \exp(-\beta h\nu)}, \end{aligned} \quad (2.40)$$

where the last identity is obtained from the limit of the geometric series $\sum_{i=1}^{\infty} x^i = (1 - x)^{-1}$ [11]. The harmonic oscillator partition function is the only one in the rho approach which can be evaluated directly and without any approximation (compare the integral substitution in the case of the translational and rotational partition functions), but the treatment of molecular vibrations as harmonic oscillations is an approximation in itself. The generalization of Eq. 2.40 to the $(3M - 6)$ vibrational degrees of freedom of a non-linear polyatomic molecule is straightforward and can be done in terms of the harmonic approximation. Following the reasoning from Sect. 2.1.2.1, the vibrational amplitudes are small compared to the overall molecular dimensions in most cases, and the vibrational motion of the M nuclei can thus be approximated as a movement in a harmonic potential around an equilibrium configuration [1]. The coupled $(3M - 6)$ -dimensional Schrödinger equation for this problem can be efficiently decoupled into $(3M - 6)$ exactly solvable one dimensional harmonic oscillator Schrödinger equations via a normal mode analysis. The normal mode analysis is an orthogonal coordinate transformation which diagonalizes the Hessian, thereby eliminating the dependency of a given vibration from all the other vibrations in the harmonic potential [4]. In the normal coordinate representation, the vibrational Hamilton operator $\hat{h}_{\text{vib}}$ is thus given as a sum of single mode harmonic oscillator Hamilton operators, and according to the reasoning leading to Eq. 2.18 the polyatomic vibrational partition function can be expressed as a product of the single mode contributions

$$q_{\text{vib}}(T) = \prod_{k=1}^{3M-6} q_{k,\text{ho}} = \prod_{k=1}^{3M-6} \frac{\exp(-\frac{1}{2}\beta h \nu_k)}{1 - \exp(-\beta h \nu_k)}, \quad (2.41)$$

where ν_k denotes the frequency of the k th normal mode. According to Eq. 2.41, the calculation of the polyatomic harmonic oscillator partition function can be carried out if the normal mode frequencies $\{\nu_k\}$ are known. The normal mode analysis is a standard procedure of quantum chemistry and implemented in many quantum chemical codes [12, 13], so that the direct computation of q_{vib} is normally possible without any significant problems. However, one should keep in mind that Eq. 2.41 is derived from the harmonic approximation and that possible anharmonic corrections applied in the calculation of the frequencies also have to be considered in the computation of q_{vib} .

2.1.2.5 Electronic Partition Function

In complete analogy to the previous degrees of freedom, the electronic partition function is given as the sum over the molecular electronic ground state as well as all excited states according to

$$q_{\text{el}}(T) = \sum_w \exp(-\beta \epsilon_w). \quad (2.42)$$

There is no simple model system which could provide the molecular energy states ϵ_w as a function of the quantum number w . Different quantum chemical methods give analytic expressions for the energy eigenvalues of the electronic Schrödinger equation on the basis of the Born-Oppenheimer approximation, but in general these equations are quite complex and have to be solved iteratively [9]. Therefore, an exact calculation of the sum in Eq. 2.42 is not possible, but since the excited electronic states in most cases are separated from the ground state by energy gaps large compared to the thermal energy at ambient temperatures, it is generally sufficient to consider only the first few or even only the first term of the series. A commonly encountered problematic case for this approach are the halogen atoms, which show first excited states less than 0.1 eV above the ground state [1]. However, sample calculations show that even in these cases it is sufficient to consider only the first terms in Eq. 2.42 [11]. This approach in a way reverses the reasoning in the derivation of the translational and rotational partition functions and can be understood as a “reversed high temperature limit” as it gets more inaccurate as the temperature increases.

As in the case of the rotational degrees of freedom, a possible degeneracy of the electronic states has to be considered in the evaluation of the electronic partition function. If the w th energy state is degenerated by a factor g_w and the electronic ground state of the molecule is set to zero, the electronic partition function can be expressed as

$$q_{\text{el}} = g_1 + g_2 \exp(-\beta \Delta \epsilon_{1,2}) + \dots, \quad (2.43)$$

where $\Delta \epsilon_{1,2}$ denotes the energy difference between the first excited state and the ground state.

2.1.2.6 Symmetry Constraints and the High Temperature Limit

The quantum mechanical treatment of the non-interacting N -particle problem in Sect. 2.1.1 explicitly excluded possible symmetry constraints. However, all known particles are either classified as bosons (wave function of an identical N -particle system is symmetric under interchange of two particles) or fermions (wave function of an identical N -particle system is antisymmetric under interchange of two particles) [5]. The distribution of independent identical fermions over the single particle states is restricted insofar as no two fermions can occupy the same state, thereby introducing additional constraints to the composition of the N -particle energy states $\{E_j\}$ from the single particle states $\{\epsilon_k\}$, see Eqs. 2.13 and 2.14. Even in the case of bosons for which no occupation limit of a given single particle state exists, the correct enumeration of microstates is still not trivial in the case of indistinguishable particles. For both the classical as well as the quantum mechanical case, the transition from the distinguishable to the indistinguishable N -particle system in Sect. 2.1.1 is achieved by neglecting the number of permutations $N!$ which are no longer distinguishable in the case of indistinguishable particles.

However, the number of distinct permutations is only equal to $N!$ if each of the N particles occupies a different energy state ϵ_k , i.e., if the same condition as in the case of fermions is fulfilled. This can be seen most directly by considering the case where $N - 1$ bosons occupy the same state (e.g. ϵ_m) and one boson occupies another state (e.g. ϵ_n). If the particles are distinguishable, there are N possible choices for the particle occupying state ϵ_n , and the number of redundant permutations one would have to consider for the transition to indistinguishable particles is thus N and not $N!$. This clearly indicates that the division by $N!$ is only exact in the limiting case of individually occupied single particle states, the condition which also has to be satisfied in the case of an N -particle fermion system. Nevertheless, Eq. 2.20 is applicable in most cases due to the same reasoning already encountered in the derivation of the translational and rotational partition functions, namely the high temperature limit. At almost all conditions except the lowest temperatures and the highest densities, the number of available single particle states exceeds the number of particles N significantly, thereby ensuring that in most cases each particle will be in a different state and that the division by $N!$ is correct. These cases for which Eq. 2.20 is valid are said to obey Boltzmann statistics [1]. The underlying assumptions of Boltzmann statistics will become more and more probable with increasing temperature, e.g. for a particle of mass $m = 10^{-25}$ kg confined to a cubic box of 0.1 m length at $T = 300$ K the number of translational states alone is of the order of 10^{30} [1].

The reasoning presented so far indicates that Boltzmann statistics is applicable to most problems at ordinary conditions, and all further derivations and results presented in this thesis are based on this approximation. For the sake of completeness it is mentioned that the exact treatment of the symmetry constraint of bosonic and fermionic N -particle systems can be accomplished and that the resulting equations are referred to as Bose–Einstein statistics and Fermi–Dirac statistics, respectively [6].

2.2 The Quantum Cluster Equilibrium Approach

2.2.1 Essentials

2.2.1.1 The Ideal Cluster Gas

The rigid rotor harmonic oscillator (rrho) model presented in the last section constitutes a well-established approach for the calculation of thermodynamic quantities on the basis of atomistic calculations. However, since it is based on the factorization of the N -particle partition function Q into the molecular partition functions q which is only exact for a non-interacting system, the rrho model can be expected to be a reasonable approximation in the case of dilute gases only, for which the interparticle interaction is comparatively small. A possible first step for the extension of the standard rrho model to interacting systems can be realized by

including interparticle interactions into the single particle unit for which the “single particle” partition function q is computed, i.e., by extending the molecular unit to a multi-molecular unit, which will be called a “cluster” from now on. Thus, in this way a cluster is defined as a molecular or atomic aggregate which is held together by some form of (attractive) interaction. This interaction could for instance be primarily coulombic in nature (e.g. in the case of sodium chloride clusters), but non-covalent interactions like hydrogen bonding (water clusters) or dispersion interactions (noble gas clusters) are thinkable as well. This approach transfers the interparticle interaction into the fundamental unit partly and in a local way. The cluster as the new fundamental unit will most generally be treated as the single molecule in the case of the conventional rrho approach, but in most cases there will be two different levels of interaction present within the cluster: the true *intramolecular* interactions which form the single molecule the cluster is composed of and which are most often covalent in nature, and the less strong *intermolecular* interactions, which are transferred into the cluster (thereby becoming *intracluster* interactions) and which ensure that the cluster as an aggregate of molecules will be stable. This classification is of course artificial: in the quantum chemical calculation of a cluster, only the type and position of the nuclei as well as the number of electrons enter, and no distinction between different molecules is made. It is also obvious that in the case of atomic clusters this classification is unnecessary, since only the interatomic interactions are present.

The combination of this new reference level with the ideas and approximations from the rrho approach is straightforward. Before, the fundamental units were molecules which have been constructed from atoms, thereby introducing rotational and vibrational degrees of freedom. Now, the fundamental units are clusters which are constructed from molecules, and since a cluster can be understood as a single “supermolecule”, no additional degrees of freedom are necessary. Thus, in complete analogy to the molecular partition function from the last section a cluster partition function is now considered, which can be factorized according to the set of rrho approximations

$$q_j = q_{j,\text{el}} q_{j,\text{trans}} q_{j,\text{rot}} q_{j,\text{vib}}, \quad (2.44)$$

where j is a cluster label which will become important later on. The partition functions for the different degrees of freedom on the right hand side of Eq. 2.44 are evaluated according to the formulas derived in the last section, for which the corresponding cluster quantities are used (e.g. the mass of the cluster for $q_{j,\text{trans}}$ and the frequencies of the cluster normal modes for $q_{j,\text{vib}}$). This approach is straightforward and allows an easy computation of the cluster partition function q_j . However, one has to be careful in the case of the comparison between different sized clusters, for instance if the change of a thermodynamic variable for the reaction of two smaller clusters to a larger one is of interest. In such a case, the number of the different kinds of cluster degrees of freedom will change, and since the degrees of freedom are treated by different approximations as presented in the last section, there will be an artificial effect arising due to the different accuracy of

the approximations employed. Consider for instance two water molecules which form a dimer cluster. Taken together, the two molecules have six translational and rotational degrees of freedom, but the dimer only has three of each of them. In contrast, the number of vibrations in the dimer is 12, whereas both molecules only possess 6 vibrational degrees of freedom. Thus, in the dimer three hindered translations and three hindered rotations will be treated as harmonic vibrations, and the question arises if the harmonic approximation is as accurate for hindered translations/rotations as the model of the particle in a box for free translations or the rigid rotor for free rotations. These questions will be examined in greater detail in [Chap. 3](#).

If only clusters of a certain type j (e.g. of a certain size) are considered, the canonical partition function for a non-interacting n -particle system of these (indistinguishable) clusters in complete analogy to [Eq. 2.20](#) is given as

$$Q_j(n_j, V, T) = \frac{q_j^{n_j}(V, T)}{n_j!}. \quad (2.45)$$

Even if all *intercluster* interactions (i.e., interactions *between* the clusters) are neglected in [Eq. 2.45](#), it is certainly an improvement over the conventional rrho model in the modeling of a condensed system, since the *intermolecular* interactions of the true system are partly accounted for within the cluster via the quantum chemical calculation, and this fraction of interactions considered will become larger as the cluster size increases. An even more detailed approach would consider not only one certain cluster species j , but many different of them, which could resemble different structural patterns occurring in the real condensed phase one is trying to model. Among them one might also include the single *molecular* monomer, since this isolated structure could occur in the real system from time to time, especially in systems showing strong structural fluctuations. These different cluster structures $\{j\}$ will certainly be distinguishable from each other (e.g., by their size), and according to that the total N -particle partition function for an ideal mixture of these different cluster species is obtained as (see also [Eq. 2.18](#)) [[14](#), [15](#)]

$$Q(N, V, T) = \prod_j Q_j(n_j, V, T) = \prod_j \frac{q_j^{n_j}(V, T)}{n_j!}, \quad (2.46)$$

where n_j now denotes the *cluster population* of the corresponding cluster species j . To make sure that [Eq. 2.46](#) is valid, one has to establish a relation between the total number of particles N and the cluster populations $\{n_j\}$. For instance, the total number of particles N could be equal to the number of *molecular* monomers in the system, which would be suitable for the calculation of thermodynamic quantities for, e.g., one mole of water molecules. In this case, the relation between N and the set $\{n_j\}$ is given by

$$N = \sum_j i_j n_j, \quad (2.47)$$

where i_j denotes the number of monomer units in the cluster species j . From the considerations presented so far, there is no simple way for the determination of the cluster populations $\{n_j\}$. As a starting option, the N molecular monomers could be distributed evenly among the different cluster species $\{j\}$, and from the partition function (Eq. 2.46) the free energy of the system could be obtained. Changing the distribution $\{n_j\}$ slightly and recalculating the free energy would then yield information about whether the change in population has a stabilizing or a destabilizing effect on the system. If there is information available on the relative abundance of a certain structural pattern over another (e.g., the relative stability of two modifications), these could be employed as well.

Even if the sketched approach will be superior to the conventional rrho model in most cases, the accurate modeling of condensed phases will have to include cluster–cluster interactions which will become more and more important at increasing densities. Furthermore, the volume of the particles will no longer be negligible at these conditions. An approximate treatment of these factors will be presented in the following.

2.2.1.2 The van der Waals Cluster Gas

The ideal cluster gas model derived in the previous part would in principle be able to treat a larger and larger fraction of interparticle interactions as the considered cluster sizes increase, but due to computational limitations there will be restrictions on the cluster sizes and therefore surface effects will always be present. A more convenient way for the treatment of additional interactions lies in a non-local mean field approach as realized in the model of van der Waals gases [11]. In this approach, the gas particles are no longer treated as point particles, but are assigned a non-zero size via a volume parameter b , and the (attractive) interparticle interaction is introduced in terms of a reduced pressure of the gas on the walls of the container which is governed by the mean field parameter a . Thus, an extension of the conventional rrho model on the basis of the van der Waals gas will have to consider the volume of the particles as a function of b as well as some form of interparticle mean field interaction as a function of a . The treatment of the reduced volume effect is achieved in a straightforward way by assigning a cluster volume V_j to each cluster species j and considering the occurrence of this cluster species in terms of the corresponding cluster populations n_j . The total excluded volume V_{ex} is thereby given as the weighted sum over all cluster species according to [14, 15]

$$V_{\text{ex}} = b_{\text{xv}} \sum_j n_j V_j, \quad (2.48)$$

where b_{xv} is a proportionality constant through which the cluster volume estimates V_j can be corrected in an average fashion. This is important, since the volume of a particle is no direct observable and there is no straightforward way of calculating the numbers $\{V_j\}$ [14]. In the present thesis as well as in many applications, the

cluster volume V_j is estimated as the sum of the atomic sphere volumes of the different atoms contributing to the cluster j , which in turn are obtained from the corresponding van der Waals radii [16, 17]. A more elaborate treatment of the cluster volumes could be obtained in terms of the GEPOL algorithm [18]. The excluded volume term calculated in this way subsequently has to be employed for the correction of the overall volume available to the N -particle system. The approximations introduced in Sect. 2.1.2 demonstrate that the translational partition function $q_{j,\text{trans}}$ is the only contribution to $Q(N, V, T)$, which depends on the volume and that the dependancy is that of a simple linear relation (see Eq. 2.30). According to that, the translational partition function corrected for the excluded volume is given as [14, 15]

$$q_{j,\text{trans}} = \left(\frac{2\pi m k_B T}{h^2} \right)^{3/2} (V - V_{\text{ex}}) = \frac{\Delta V}{\Lambda^3}. \quad (2.49)$$

The attractive mean field interaction between the clusters is considered in a similar way. According to Eq. 2.43, a common zero-of-energy reference has to be established first for the different cluster types $\{j\}$, which in most cases is set to the ground state energy of the relaxed (molecular) monomer unit. A physically reasonable energy scale for the ordering of the larger cluster structures is then obtained by considering the difference in the total ground state energy $E_{j,\text{tot}}$ of a cluster j and i_j -times the ground state energy of the relaxed monomer unit $E_{1,\text{tot}}$

$$\Delta E_{j,\text{intra}} = E_{j,\text{tot}} - i_j E_{1,\text{tot}}, \quad (2.50)$$

where i_j again denotes the number of monomer units in cluster j . Energy differences of the form as in Eq. 2.50 are frequently encountered in quantum chemical applications and are referred to as *total/supramolecular interaction energies* or *interaction energies according to the supramolecular approach* [19]. Due to the limited basis sets normally applied in the actual quantum chemical calculation of these energies, a treatment of the basis set superposition error (bsse) is often reasonable, for instance via the counterpoise correction scheme [20]. In addition to this *intracuster* energy contribution, the van der Waals-like mean field interaction *between* the clusters is accounted for via a potential term of the form

$$\Delta E_{j,\text{inter}} = -\frac{a_{\text{mf}} i_j}{V}, \quad (2.51)$$

where a_{mf} is an additional empirical parameter adjusting the strength of the intercluster interaction. As in the case of the classical van der Waals model, the factor i_j/V can be understood as a number density of the monomer units in cluster j per volume of the N -particle system. The sum of these two interaction energy terms is subsequently employed in the computation of the electronic cluster partition function $q_{j,\text{el}}$ according to [14, 15]

$$q_{j,\text{el}} = \exp[-\beta(\Delta E_{j,\text{intra}} + \Delta E_{j,\text{inter}})] = \exp\left[-\beta\left(\Delta E_{j,\text{intra}} - \frac{a_{\text{mf}} i_j}{V}\right)\right], \quad (2.52)$$

see also Eq. 2.42. From this derivation it is clear that in contrast to the conventional case in Eq. 2.42 true excited states of the monomer units or the clusters are not considered and that the applied energy “states” are referring to the binding situation within a cluster as well as the mean field interaction to the other clusters. Furthermore, it is apparent that the energy contributions in contrast to Eq. 2.43 are of a stabilizing origin, i.e., both the intracluster interaction energy (Eq. 2.50) as well as the intercluster interaction energy (Eq. 2.51) are negative, which results in electronic contributions to the overall cluster partition function larger than one. From a pure energetic point of view larger clusters exhibiting larger absolute values in both $\Delta E_{j,\text{intra}}$ and $\Delta E_{j,\text{inter}}$ are thus favored via the electronic contribution to the cluster partition function.

The presented van der Waals extension of the rrho model involves the introduction of two new parameters a_{mf} and b_{xv} , which can be understood as direct analogs to the van der Waals parameters a and b . There is no straightforward rule for the evaluation of these parameters on the basis of first principles methods, and the most convenient way of determining these unknowns is fitting some calculated thermodynamic quantity to an experimental reference. In this thesis the chosen reference quantity will normally be the molar volume, and the employed fitting procedure is a straightforward application of the commonly used least-squares fit criterion. According to that approach, a set of test isobars is computed over a predefined $a_{\text{mf}}/b_{\text{xv}}$ grid, and the absolute difference of each of these test curves to the (experimental) reference isobar is accumulated in an error vector of the form

$$\Delta \mathbf{V}(a_{\text{mf}}, b_{\text{xv}}) = [V_{\text{ref}} - V_{a_{\text{mf}}, b_{\text{xv}}}]_{T_{\text{min}} \dots T_{\text{max}}}, \quad (2.53)$$

where V_{ref} , $V_{a_{\text{mf}}, b_{\text{xv}}}$ denote the molar reference volume and the volume of one of the test isobars at a given temperature, respectively, and the vector $\Delta \mathbf{V}$ has as many components as the number of sampled temperature points [17]. In a subsequent analysis the Euclidean norm $\|\Delta \mathbf{V}\|$ of each sampled vector $\Delta \mathbf{V}$ is computed, and the test isobar yielding the smallest norm is considered to be the most accurate approximation to the experimental reference. In the following, the Euclidean norm of the error vector $\|\Delta \mathbf{V}\|$ will also synonymously be denoted as the accuracy of the underlying test isobar [21, 22].

2.2.1.3 Cluster Equilibrium

The methodology presented so far covers the treatment of particle interactions on an accurate local scale (intracluster interactions via first principles computations) and an approximate non-local scale (intercluster interactions via a van der Waals-like mean field term) as well as the approximate treatment of the excluded volume in terms of atomic van der Waals radii. However, in order to obtain thermodynamic information for the N -particle system, the N -particle partition function (Eq. 2.46) has to be evaluated, which is only possible if the underlying cluster populations $\{n_j\}$ are known. In addition to the empirical suggestions made earlier,

an algorithmic way for solving the population equations on the basis of a thermodynamic equilibrium between the different clusters has been developed in the late nineties of the last century [14].

The underlying equilibrium reaction takes into account the formation of all clusters in the set $\{C_j\}$ from the basic monomer unit C_1 according to [14, 15]

$$C_1 \rightleftharpoons \frac{C_2}{2} \rightleftharpoons \dots \rightleftharpoons \frac{C_j}{i_j} \rightleftharpoons \dots \rightleftharpoons \frac{C_\eta}{i_\eta}, \quad (2.54)$$

where η denotes the largest cluster in the set and i_η equals the number of monomers in this cluster. If the equilibrium in Eq. 2.54 is assumed to be a thermodynamic equilibrium, the change in free energy A [1]

$$dA = -SdT - pdV + \sum_j \mu_j dn_j \quad (2.55)$$

has to be zero, where μ_j denotes the chemical potential of cluster j . At the conditions of the canonical ensemble (constant volume, constant temperature, constant particle number) this criterion is identical to the equality of the various chemical potentials $\{\mu_j\}$, i.e., Eq. 2.54 translates to

$$\mu_1 = \frac{\mu_2}{2} = \dots = \frac{\mu_j}{i_j} = \dots = \frac{\mu_\eta}{i_\eta}. \quad (2.56)$$

The chemical potential of a species j can most generally be expressed as a function of the canonical partition function Q according to [16]

$$\mu_j = -k_B T \left(\frac{\partial \ln(Q)}{\partial n_j} \right)_{n_{k \neq j}, V, T} \approx -k_B T \ln \left(\frac{q_j}{n_j} \right), \quad (2.57)$$

where the final transformation involves the application of Stirling's approximation [23]. The relation expressed in Eq. 2.57 provides a simple connection between the chemical potential μ_j and the population n_j of a given cluster j , and the substitution of the chemical potentials in Eq. 2.56 according to Eq. 2.57 yields a direct relation between the populations n_j , n_k of two different cluster species j and k . If one of these species (conveniently the monomer, $i_k = 1$) is set as a reference, the population of all remaining clusters can be expressed as functions of this reference population

$$\begin{aligned} n_j &= q_j \left[\frac{n_k}{q_k} \right]^{(i_j/i_k)} N_A^{(i_j-1)} \\ &= q_j \left[\frac{n_1}{q_1} \right]^{(i_j)} N_A^{(i_j-1)}. \end{aligned} \quad (2.58)$$

According to this approach, the problem of finding η populations is reduced to the determination of the reference population n_1 . In order to obtain an equality for this reference population, the particle conservation condition in combination with a

fixed total number of particles as expressed in Eq. 2.47 is employed. The substitution of the various populations in Eq. 2.47 according to Eq. 2.58 finally results in a polynomial equation in the monomer population n_1 , which takes the form

$$0 = -N + \sum_{j=1}^{\eta} \left[\frac{(i_j) q_j N_A^{(i_j-1)}}{q_1^{(i_j)}} \right] n_1^{(i_j)}. \quad (2.59)$$

Without loss of generality, the total number of particles N can be fixed to one mole, and according to the fundamental theorem of algebra there will be i_η different possible monomer population roots to Eq. 2.59 [24]. However, only roots from the real field are expected to be physically reasonable, and all complex solutions to Eq. 2.59 are discarded, but in the general case there will also be several real roots satisfying Eq. 2.59. Each of these roots can be employed to compute a complete cluster distribution on the basis of Eq. 2.58, which finally results in up to i_η possible cluster distributions (“phases”) at the chosen state point. The stable phase at the applied conditions will be the one minimizing the free energy of the system, e.g., if the total particle number N , the temperature T , and the pressure p (instead of the volume V) are fixed, the related free energy will be the Gibbs free energy G , which can be obtained from the partition function Q according to³

$$G = -k_B T \ln(Q) + pV, \quad (2.60)$$

i.e., in order to evaluate the free energy, the volume of the different phases has to be obtained first. A straightforward way to this end exploits the relation between the (fixed) pressure p of the system and the canonical partition function $Q(N, V, T)$ [1, 14, 15]

$$p = kT \left(\frac{\partial \ln(Q)}{\partial V} \right)_{N,T}. \quad (2.61)$$

The contributions to the partition function Q which depend on the volume V are the translational partition function $q_{j,\text{trans}}$ and the electronic partition function $q_{j,\text{el}}$, see Eqs. 2.49 and 2.52. The evaluation of the derivative in Eq. 2.61 thus results in [16]

$$p = \frac{\sum_j^{\eta} (k_B T n_j V^2 - a_{\text{mf}} i_j n_j \Delta V)}{V^2 \Delta V}, \quad (2.62)$$

³ In principle one has to consider the isothermal–isobaric partition function $Q(N, T, p) = \sum_j \sum_V \exp(-\beta E_j) \exp(-\beta pV)$ for these thermodynamic reference variables, but since both summations are uncoupled, the pressure–volume term can be evaluated directly, yielding Eq. 2.60 [1].

where $\Delta V = V - V_{\text{ex}}$ (see Eq. 2.49). Besides the volume V , this equation only contains known quantities and therefore can be rearranged to a polynomial equation in V taking the form

$$0 = [-p]V^3 + \left[k_{\text{B}}T \sum_j^{\eta} n_j + pV_{\text{ex}} \right] V^2 - \left[a_{\text{mf}} \sum_j^{\eta} i_j n_j \right] V + \left[a_{\text{mf}} \sum_j^{\eta} i_j n_j \right] V_{\text{ex}}. \quad (2.63)$$

The coefficients of this polynomial equation depend on the cluster population distribution $\{n_j\}$, which means that for each of the different population sets up to three possible volumes can be obtained (the actual number is again equal to the number of real roots of Eq. 2.63). In combination with the population distributions, these volumes are employed for the determination of the stable phase at the chosen pressure p and temperature T according to Eq. 2.60, i.e., the population–volume combination which yields the minimum in G is considered to be the stable phase. The population set obtained in this way can subsequently be employed for the computation of the canonical partition function according to Eq. 2.46.

The above sketched scheme constitutes an algorithmic approach for the determination of the cluster distribution set and the phase volume of the stable phase at the chosen pressure–temperature conditions, which is readily implemented in a computer program [14, 16, 25]. However, in order to compute the coefficients of the population polynomial (Eq. 2.59), the cluster partition functions $\{q_j\}$ have to be available, but according to Eqs. 2.49 and 2.52 the translational and electronic contribution to each q_j depend on the volume V , which cannot be calculated until the populations are known, see Eq. 2.63. These mutual dependencies require an iterative procedure, in which a self-consistent set of cluster partition functions $\{q_j\}$, cluster populations $\{n_j\}$, and volume V is determined. The flow chart of the core iteration procedure implemented in the PEACEMAKER code is illustrated in Fig. 2.1 [16, 25]. The first step of the iteration consists of the computation of the cluster partition functions q_j , which depend on the phase volume V and also on the cluster populations $\{n_j\}$ via the excluded volume correction term, see Eq. 2.48. This means that in order to start the iteration, there are two initial guesses to be made, one for the volume V and one for the populations $\{n_j\}$. Depending on whether the current p, T state point is the first one of the calculation or an intermediate one, the initial guesses are either obtained by setting the volume V to the volume of an ideal gas at the chosen conditions and by distributing the number of monomer units C_1 uniformly over the different clusters according to Eq. 2.47 (i.e., $n_j = (i_j \eta)^{-1}$), or by constructing linear combinations of the volume and the populations obtained from previously converged iterations and the ideal gas volume and uniform distribution, respectively.

The next step includes the computation of the population polynomial coefficients, which according to Eq. 2.59 depend on the previously calculated cluster

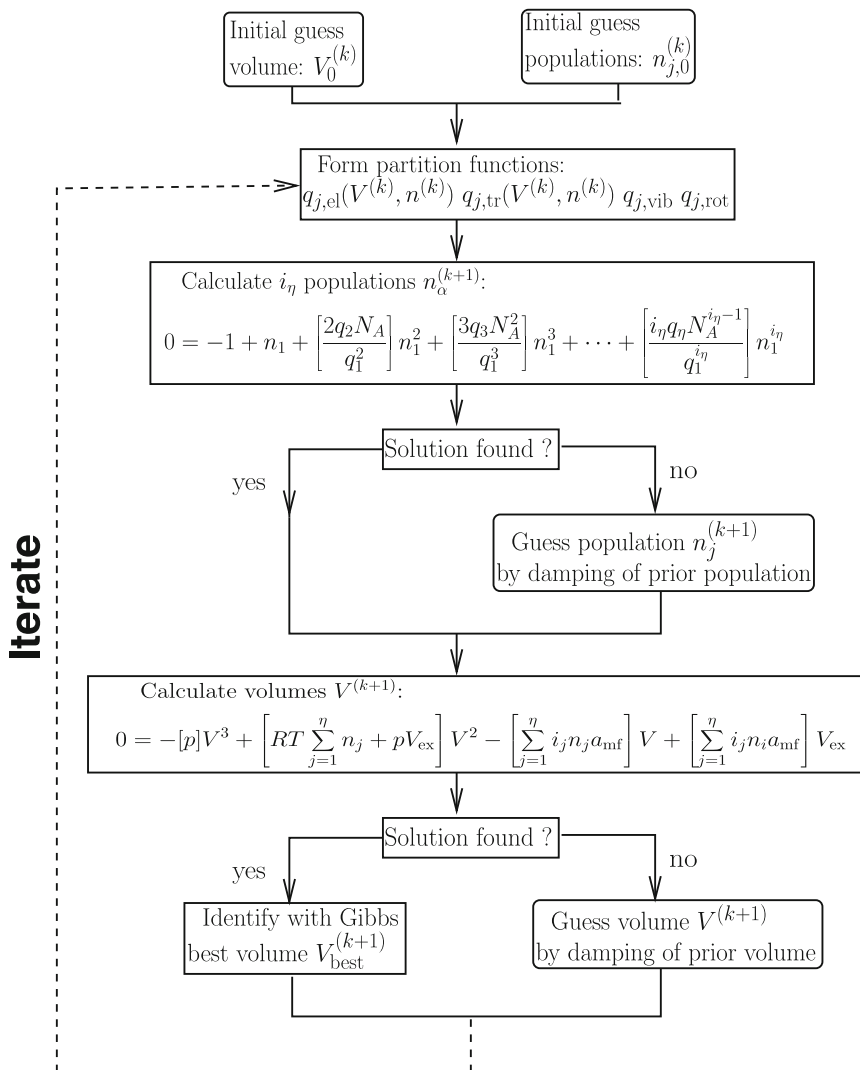


Fig. 2.1 Flowchart of the PEACEMAKER iteration procedure.⁴

partition functions. From the (real) roots of the population polynomial possible cluster population distributions $\{n_j\}$ are obtained (see Eq. 2.58), which are subsequently used for setting up the coefficients of the volume polynomial (Eq. 2.63). During the final step of each iteration, the Gibbs energy of all valid

⁴ Reprinted with permission from Ref. [16]. Copyright 2005, American Institute of Physics

population–volume combinations is computed and the stable phase for the given p , T state point is identified. This population set and the corresponding volume reenter the cycle as the new guess for the next iteration. The quantity which is used to check the convergence of the iteration procedure is chosen to be the phase volume V in the PEACEMAKER code, but the populations $\{n_j\}$ or the partition function Q could be employed for this purpose as well [16, 25].

The algorithmic approach for the computation of the cluster populations of the van der Waals cluster gas introduced above is known as the *quantum cluster equilibrium* (*qce*) model in literature [14–16]. All relevant information required for a qce calculation can be obtained from static first principles calculations of the different cluster structures which are included in the equilibrium reaction, see Eq. 2.54.

2.2.2 Thermodynamics from Quantum Cluster Equilibrium Calculations

The quantum cluster equilibrium model introduced in the last section enables the computation of a self-consistent canonical partition function Q for the van der Waals cluster gas if a set of cluster structures (and corresponding properties like moments of inertia and harmonic frequencies) as well as a state point in the temperature–pressure space are specified as input values. Once the partition function is available, the computation of thermodynamic quantities is achieved in a straightforward manner, since all thermodynamic quantities can be expressed as analytical functions of the partition function Q . An example for such a relation has already been encountered in the derivation of the qce approach itself, namely the relation between the Gibbs free energy G (see Eq. 2.60) or the pressure p (see Eq. 2.61) and the partition function Q .

In all cases relevant for this thesis the functional dependency between a quantity O and the partition function Q is of the form $O = f(\ln(Q))$, compare Eqs. 2.57, 2.60, and 2.61. This fact, combined with the particular form of the qce partition function (see Eq. 2.46) makes it possible to express the quantity O in terms of the cluster populations $\{n_j\}$ and the cluster partition functions $\{q_j\}$ instead of the N -particle partition function Q , thereby avoiding the computation of Q via a cumbersome evaluation of the $n_j!$ terms in Eq. 2.46 at all. Again, this observation has been employed before (see Eq. 2.57) and will be demonstrated in the following using the example of the entropy [17].

The functional dependency between the entropy S and the canonical partition function Q is given by [1]

$$S = k_B \ln(Q) + k_B T \left(\frac{\partial \ln(Q)}{\partial T} \right)_{N,V}. \quad (2.64)$$

The replacement of Q in Eq. 2.64 in terms of the qce factorization from Eq. 2.46 results in

$$S = k_B \sum_{j=1}^{\eta} \ln \left(\frac{q_j^{n_j}}{n_j!} \right) + k_B T \left(\frac{\partial}{\partial T} \sum_{j=1}^{\eta} \ln \left(\frac{q_j^{n_j}}{n_j!} \right) \right). \quad (2.65)$$

In order to resolve the factorial terms in Eq. 2.65, Stirling's approximation ($\ln(n!) \approx n \ln(n) - n$) will be applied (as before in the case of the chemical potential, see Eq. 2.57), thereby yielding [23]

$$\begin{aligned} S &= k_B \left[\sum_{j=1}^{\eta} n_j (\ln q_j - \ln n_j + 1) \right] + k_B T \left[\frac{\partial}{\partial T} \sum_{j=1}^{\eta} n_j (\ln q_j - \ln n_j + 1) \right] \\ &= k_B \left[\sum_{j=1}^{\eta} n_j (\ln q_j - \ln n_j + 1) \right] + k_B T \left[\sum_{j=1}^{\eta} \frac{\partial}{\partial T} n_j \ln q_j \right]. \end{aligned} \quad (2.66)$$

The considerations presented in the last sections show that the cluster partition functions $\{q_j\}$ can be factorized into degree-of-freedom dependent contributions (see Eq. 2.44) and that these contributions are analytical functions of the temperature T (see Sect. 2.1.2), i.e., the evaluation of the temperature derivatives in the second term on the right hand side of Eq. 2.66 can be accomplished in a straightforward fashion according to

$$\begin{aligned} \left(\frac{\partial \ln q_j^{\text{trans}}}{\partial T} \right)_{N,V} &= \frac{\partial}{\partial T} \ln \left[\frac{\Delta V (2\pi m_j k_B T)^{3/2}}{h^3} \right] = \frac{3}{2T}; \\ \left(\frac{\partial \ln q_j^{\text{rot}}}{\partial T} \right)_{N,V} &= \frac{\partial}{\partial T} \ln \left[\frac{\pi^{1/2}}{\sigma} \left(\frac{T^3}{\Theta_A \Theta_B \Theta_C} \right)^{1/2} \right] = \frac{3}{2T}; \\ \left(\frac{\partial \ln q_j^{\text{vib}}}{\partial T} \right)_{N,V} &= \frac{\partial}{\partial T} \ln \left[\prod_k^{3M-6} \frac{\exp\left(-\frac{\beta h \nu_k}{2}\right)}{1 - \exp(-\beta h \nu_k)} \right] \\ &= \sum_k^{3M-6} \frac{h \nu_k}{2 k_B T^2} + \frac{\frac{h \nu_k}{k_B T^2}}{\exp(\beta h \nu_k) - 1}; \\ \left(\frac{\partial \ln q_j^{\text{el}}}{\partial T} \right)_{N,V} &= \frac{\partial}{\partial T} \ln \left[\exp \left(\frac{-\Delta E_{j,\text{intra}} + i_j a_{\text{mf}} V^{-1}}{k_B T} \right) \right] \\ &= - \frac{-\Delta E_{j,\text{intra}} + i_j a_{\text{mf}} V^{-1}}{k_B T^2}. \end{aligned} \quad (2.67)$$

The insertion of the degree-of-freedom dependent temperature derivatives from Eq. 2.67 in Eq. 2.66 leads to the final qce entropy expression [17]

$$\begin{aligned}
S = & k_B \sum_j^\eta n_j (\ln q_j - \ln n_j + 1) \\
& + k_B T \sum_j^\eta n_j \left[\frac{\Delta E_{j,\text{intra}} - i_j a_{\text{mf}} V^{-1}}{k_B T^2} + \left(\sum_k^{3M-6} \frac{h\nu_k}{2k_B T^2} + \frac{\frac{h\nu_k}{k_B T^2}}{\exp\left(\frac{h\nu_k}{k_B T}\right) - 1} \right) + \frac{3}{T} \right].
\end{aligned} \tag{2.68}$$

The necessary quantities which have to be available for the entropy calculation according to Eq. 2.68 are the cluster populations $\{n_j\}$, the cluster partition functions $\{q_j\}$, and the cluster properties which are also needed to calculate the set $\{q_j\}$. As a second example, the equality for the qce isochoric heat capacity is given, which can be computed according to [26]

$$\begin{aligned}
C_v = & \left(\frac{\partial U}{\partial T} \right)_{N,V} = 2k_B T \left(\frac{\partial \ln(Q)}{\partial T} \right)_{N,V} + k_B T^2 \left(\frac{\partial^2 \ln(Q)}{\partial T^2} \right)_{N,V} \\
= & 2k_B T \sum_j^\eta n_j \frac{\partial}{\partial T} \ln(q_j) + k_B T^2 \sum_j^\eta n_j \frac{\partial^2}{\partial T^2} \ln(q_j),
\end{aligned} \tag{2.69}$$

where the temperature derivatives of the cluster partition functions can be evaluated in an analytical way as in the case of the entropy, see Eq. 2.67. In complete analogy to the approach which led to Eq. 2.68, analytical equations for all the other relevant thermodynamic quantities can be derived on the basis of the qce partition function in Eq. 2.46. Although the qce partition function is based on a non-interacting van der Waals cluster gas and thereby is of a profoundly approximate nature concerning the treatment of real condensed systems, the calculation of thermodynamic properties in the frame of the qce approach is realized in an analytically exact way (with the exception of Stirling's approximation), which can be considered to be one of the most important advantages of this method. The availability of an analytical partition function is not given in most other approaches suitable for the treatment of condensed phase thermodynamics, and in many cases such approaches have to rely on approximate relations for the relevant thermodynamic quantities depending on additional parameters or on the computational details, e.g., the simulation length [27–29]. Some of these approaches will be outlined briefly in the next section.

2.3 Thermodynamic Data from Molecular Dynamics Simulations

2.3.1 Equilibrium Methods

In contrast to the static approaches discussed in the preceding sections, molecular dynamics (md) simulations explicitly account for the microscopic dynamics of the

investigated system, i.e., each md simulation evolves on a real time axis. In the case of an equilibrium md simulation, thermodynamic constraints are placed on the system according to the thermodynamic nature of the process being investigated, for instance one would fix the number of particles N , the volume V , and the temperature T in the case of an isochoric system being in equilibrium with a heat bath. A md simulation in this setup is equivalent to sampling the canonical (N, V, T) ensemble, for which the relevant thermodynamic potential is the Helmholtz free energy A given by

$$A = -k_B T \ln(Q(N, V, T)). \quad (2.70)$$

As outlined above, both the rrho as well as the qce approach are fundamentally linked to the factorization of the N -particle partition function Q into single particle contributions, thereby ignoring all interparticle interactions as a first approximation. However, md simulation methods explicitly incorporate interparticle interactions via an interaction potential $U(\mathbf{q})$, which is either obtained from electronic structure calculations on the fly (*first principles* molecular dynamics (fpmd) simulations) [30, 31] or from an analytical force field function (traditional molecular dynamics simulations) [32]. Thus, an ideal-gas-like factorization approach for the determination of Q cannot be brought in line with the basic methodology of md simulations. On the other hand, a direct evaluation of the N -particle partition function is prohibitively difficult, which demonstrates the need for a fundamentally different approach.

In most cases, it is not necessary to calculate the absolute value for, e.g., A according to Eq. 2.70 in order to extract the relevant thermodynamic information, since most chemical processes involve a change from a well-defined initial state 1 to a final state 2, and it is often sufficient to have access to the change of a thermodynamic quantity during the reaction course $1 \rightarrow 2$. If the quantity of interest is the free energy change ΔA , Eq. 2.70 reduces to

$$\Delta A = A_2 - A_1 = -k_B T \ln\left(\frac{Q_2}{Q_1}\right), \quad (2.71)$$

and if the masses of the particles do not change during the process $1 \rightarrow 2$, Eq. 2.5 can be employed to obtain

$$\Delta A = -k_B T \ln\left(\frac{Z_2}{Z_1}\right). \quad (2.72)$$

This equation indicates that the new target quantity is the ratio Z_2/Z_1 , which often is still too complicated to calculate for systems with many degrees of freedom if no further treatment is applied, and the largest part of this section will be devoted to transformations of Eqs. 2.71 and 2.72, respectively, to expressions which can readily be combined with the methodology of md simulations. The two emerging methods covered here are referred to as free energy perturbation (fep) theory and thermodynamic integration, which are among the most frequently employed approaches for the calculation of free energy changes from md simulations today [33, 34].

One of the most powerful and universal approaches of applied mathematics is perturbation theory, which divides a problem too complicated to be exactly solvable into a (simpler) reference problem and a perturbation. In the frame of the Hamiltonian formalism introduced in Sect. 2.1.1 such a division is often realized in the following way [33]

$$\mathcal{H}_{\text{tot}}(\mathbf{p}, \mathbf{q}) = \mathcal{H}_{\text{ref}}(\mathbf{p}, \mathbf{q}) + \Delta\mathcal{H}(\mathbf{p}, \mathbf{q}). \quad (2.73)$$

In this equation $\mathcal{H}_{\text{tot}}(\mathbf{p}, \mathbf{q})$ refers to the Hamiltonian of the full problem (compare also Eq. 2.2), and $\mathcal{H}_{\text{ref}}(\mathbf{p}, \mathbf{q}), \Delta\mathcal{H}(\mathbf{p}, \mathbf{q})$ denote the Hamiltonian of the simpler reference problem and of the perturbation, respectively. For instance, the full problem could be a solute at infinite dilution in a solvent. In this case the reference problem $\mathcal{H}_{\text{ref}}$ could be chosen to be the unsolvated solute, and the perturbation $\Delta\mathcal{H}$ would consist of all the solute–solvent interactions⁵ [33]. Following Eqs. 2.1 and 2.71, the free energy change between the perturbed system 2 ($\mathcal{H}_2 = \mathcal{H}_{\text{tot}}$) and the reference system 1 ($\mathcal{H}_1 = \mathcal{H}_{\text{ref}}$) can be expressed as

$$\begin{aligned} \Delta A &= -k_B T \ln \left[\frac{\int \exp(-\beta \mathcal{H}_2(\mathbf{p}, \mathbf{q})) d\mathbf{p} d\mathbf{q}}{\int \exp(-\beta \mathcal{H}_1(\mathbf{p}, \mathbf{q})) d\mathbf{p} d\mathbf{q}} \right] \\ &= -k_B T \ln \left[\frac{\int \exp(-\beta \Delta\mathcal{H}(\mathbf{p}, \mathbf{q})) \exp(-\beta \mathcal{H}_{\text{ref}}(\mathbf{p}, \mathbf{q})) d\mathbf{p} d\mathbf{q}}{\int \exp(-\beta \mathcal{H}_{\text{ref}}(\mathbf{p}, \mathbf{q})) d\mathbf{p} d\mathbf{q}} \right]. \end{aligned} \quad (2.74)$$

In the frame of the (N, V, T) ensemble the probability P for the system under investigation to be in a certain energy state E_j (or to occupy a certain region of phase space $d\mathbf{p}d\mathbf{q}$ in a classical treatment) is proportional to the corresponding Boltzmann factor $\exp(-\beta E_j)$, and the proportionality constant is the inverse of the partition function Q , which ensures a normalization of the overall probability to one [6]. According to that reasoning, the probability distribution function $P_1(\mathbf{p}, \mathbf{q})$ for the reference state 1 is given as

$$P_1(\mathbf{p}, \mathbf{q}) = \frac{\exp(-\beta \mathcal{H}_1(\mathbf{p}, \mathbf{q}))}{Q(N, V, T)} \propto \frac{\exp(-\beta \mathcal{H}_1(\mathbf{p}, \mathbf{q}))}{\int \exp(-\beta \mathcal{H}_1(\mathbf{p}, \mathbf{q})) d\mathbf{p} d\mathbf{q}}. \quad (2.75)$$

With this definition, the free energy change for the process $1 \rightarrow 2$ can be formulated in terms of the probability distribution function [33]

$$\begin{aligned} \Delta A &= -k_B T \ln \left[\int \exp(-\beta \Delta\mathcal{H}(\mathbf{p}, \mathbf{q})) P_1(\mathbf{p}, \mathbf{q}) d\mathbf{p} d\mathbf{q} \right] \\ &= -k_B T \ln [\langle \exp(-\beta \Delta\mathcal{H}(\mathbf{p}, \mathbf{q})) \rangle_1], \end{aligned} \quad (2.76)$$

where the brackets $\langle \dots \rangle$ indicate a so-called *ensemble average* (and no scalar product as in the case of Sect. 2.1.1). The direct computation of the ensemble average would require the availability of the probability distribution function

⁵ Depending on the exact nature of the problem and the quantity of interest, the solvent-solvent interactions would have to be included in the perturbation term as well.

$P_1(\mathbf{p}, \mathbf{q})$ and thereby of the partition function Q (see Eq. 2.75), but under the assumption of the ergodic hypothesis an md simulation in the (N, V, T) ensemble samples the phase space of the examined system just according to the probability distribution in Eq. 2.75 and thus intrinsically provides the correct statistical weight for the average in Eq. 2.76 [29]. It should be noted that in cases where the particle masses do not change during the transformation $1 \rightarrow 2$, an identical derivation starting from Eq. 2.72 yields the equality

$$\Delta A = -k_B T \ln[\langle \exp(-\beta \Delta U(\mathbf{q})) \rangle_1], \quad (2.77)$$

where $\Delta U(\mathbf{q})$ denotes the perturbation in the potential in analogy to Eq. 2.73. The result expressed in Eqs. 2.76 and 2.77 demonstrates that in order to obtain the free energy change for the process $1 \rightarrow 2$ it is only necessary to sample the reference system 1 and to employ the obtained trajectory for the evaluation of the exponential average in Eq. 2.76. Despite this simple procedure, there might be practical problems in the evaluation of Eq. 2.76. In order to illustrate these aspects, it is helpful to rewrite Eq. 2.76 in terms of the probability distribution function of the perturbation $P(\Delta U)$, which thereby reduces to a one-dimensional integral according to [33]

$$\Delta A = -k_B T \ln \left[\int \exp(-\beta \Delta U) P_1(\Delta U) d\Delta U \right]. \quad (2.78)$$

In many cases, $P_1(\Delta U)$ will be roughly of Gaussian-like shape. However, the integrand being relevant for the free energy change is not $P_1(\Delta U)$ but the product between $P_1(\Delta U)$ and $\exp(-\beta \Delta U)$, which is also of Gaussian-like form but shifted to lower ΔU . This means that the most important contributions to the integral in Eq. 2.78 will occur with a relatively low probability in the sampling of $P_1(\Delta U)$ if the two distributions do not overlap significantly, thereby limiting the general applicability of Eqs. 2.76 and 2.77, respectively [33]. Another problem arises if the initial and final states of the system under investigation are very different in a sense that their important regions in phase space either only overlap partly or do not overlap at all. In these cases the perturbation $\Delta \mathcal{H}$ will be rather large, and an enhanced sampling procedure has to be applied. A straightforward approach considers the construction of intermediate states $\{i\}$ representing only sections of the overall process $1 \rightarrow 2$. Each of these intermediate processes can then be treated separately in terms of the fep approach, and the total change in free energy is obtained as

$$\Delta A = \sum_i \Delta A_{i,i+1} = -k_B T \ln[\langle \exp(-\beta \Delta U_{i,i+1}) \rangle_i]. \quad (2.79)$$

The second method for the calculation of free energy changes on the basis of md simulations presented here is the thermodynamic integration scheme [29, 34]. The basic idea behind this approach can be summarized as instead of calculating the free energy directly, e.g., via Eq. 2.70, the derivative of the free energy with

respect to an (arbitrary) order parameter λ is computed. This is a most natural approach which in a similar way is also employed in real experiments, where only relative changes of the free energy with respect to an external parameter (e.g. the volume) are measurable [29]. The order parameter λ can either be a function of the (generalized) coordinates of the system (e.g. the distance between two particles) or be a parameter in the Hamiltonian $\mathcal{H}$, which is used to switch a certain interaction on or off [34]. This latter variant is also referred to as an alchemical transformation (since the system can undergo significant changes during the process $1 \rightarrow 2$, see below) and it will be the one which is treated here exemplarily. The parametrization of the Hamiltonian is usually carried out in the following way

$$\mathcal{H}_\lambda(\mathbf{p}, \mathbf{q}) = (1 - \lambda)\mathcal{H}_1(\mathbf{p}, \mathbf{q}) + \lambda\mathcal{H}_2(\mathbf{p}, \mathbf{q}), \quad (2.80)$$

so that for $\lambda = 0$ the initial state 1 and for $\lambda = 1$ the final state 2 is obtained. The free energy of the system under investigation can readily be expressed in terms of this parameterized Hamiltonian via the partition function from Eq. 2.1. The derivative of this free energy expression with respect to the order parameter λ is given as

$$\frac{dA(\lambda)}{d\lambda} = \frac{\int \left(\frac{\partial \mathcal{H}_\lambda(\mathbf{p}, \mathbf{q})}{\partial \lambda} \right) \exp(-\beta \mathcal{H}_\lambda(\mathbf{p}, \mathbf{q})) d\mathbf{p} d\mathbf{q}}{\int \exp(-\beta \mathcal{H}_\lambda(\mathbf{p}, \mathbf{q})) d\mathbf{p} d\mathbf{q}}. \quad (2.81)$$

This equation is again of the form $\int O(\lambda) P_\lambda d\mathbf{p} d\mathbf{q}$ (compare Eq. 2.75) and thus can be identified as an ensemble average for $O = \partial \mathcal{H}_\lambda / \partial \lambda$. Thus Eq. 2.81 can be rewritten as

$$\frac{dA(\lambda)}{d\lambda} = \left\langle \frac{\partial \mathcal{H}_\lambda(\mathbf{p}, \mathbf{q})}{\partial \lambda} \right\rangle_\lambda, \quad (2.82)$$

and the free energy change for the process $1 \rightarrow 2$ follows from integrating Eq. 2.82 along λ according to

$$\Delta A = \int_{\lambda=0}^{\lambda=1} \frac{dA(\lambda)}{d\lambda} d\lambda = \int_{\lambda=0}^{\lambda=1} \left\langle \frac{\partial \mathcal{H}_\lambda(\mathbf{p}, \mathbf{q})}{\partial \lambda} \right\rangle_\lambda d\lambda. \quad (2.83)$$

The free energy change ΔA can thus be computed from ensemble averages of the change in the Hamiltonian under variation of λ , which are typically obtained from a series of equilibrium md simulations carried out at different values for λ between 0 and 1 [29]. This approach is a very general one and will be applicable as long as $\mathcal{H}_\lambda$ interpolates smoothly between $\mathcal{H}_1$ and $\mathcal{H}_2$. The path along which the order parameter is varied not necessarily has to be a physical one. For instance, it is possible to calculate the difference in free energy upon transformation of a functional group within a molecule into another one by gradually changing the first group into the second at different values of λ [29]. It is clear that during such a transformation the particle masses will possibly change, which is the reason for

parameterizing the full Hamiltonian (see Eq. 2.80) and not only the configurational contribution U . If, however, the particle masses stay constant during the process $1 \rightarrow 2$, Eq. 2.83 again simplifies to

$$\Delta A = \int_{\lambda=0}^{\lambda=1} \left\langle \frac{\partial U_{\lambda}(\mathbf{q})}{\partial \lambda} \right\rangle_{\lambda} d\lambda. \quad (2.84)$$

It should be noted that additional weighting factors can be included to each of the ensemble averages used to compute the free energy change according to Eq. 2.83, which help to stress the influence of certain λ -stages on the path $\lambda = 0 \rightarrow \lambda = 1$ [34].

The discussion so far concentrated on the calculation of free energy changes in the (N, V, T) ensemble, and due to the missing availability of the partition function in md simulations, there is no general approach for the computation of other thermodynamic quantities like e.g. the entropy. However, the methodologies of perturbation theory and thermodynamic integration are often applicable to other properties in a similar way. For instance, entropy differences in the (N, V, T) ensemble can be expressed in the thermodynamic integration scheme in a straightforward way following the same route as in the case of free energy changes [35]

$$\Delta S = S_2 - S_1 = \frac{1}{k_B T^2} \int_{\lambda=0}^{\lambda=1} \left[\left\langle \frac{\partial \mathcal{H}(\lambda)}{\partial \lambda} \right\rangle_{\lambda} \langle \mathcal{H}(\lambda) \rangle_{\lambda} - \left\langle \frac{\partial \mathcal{H}(\lambda)}{\partial \lambda} \mathcal{H}(\lambda) \right\rangle_{\lambda} \right] d\lambda. \quad (2.85)$$

Another approach is based on the application of classical thermodynamic relations, e.g. between the free energy A and the entropy S

$$S = - \left(\frac{\partial A}{\partial T} \right)_{N,V}, \quad (2.86)$$

which can be evaluated with the aid of Eqs. 2.70 and 2.1 according to [35]

$$\begin{aligned} S &= k_B \ln(Q) + \frac{\int \mathcal{H}(\mathbf{p}, \mathbf{q}) \exp(-\beta \mathcal{H}(\mathbf{p}, \mathbf{q})) d\mathbf{p} d\mathbf{q}}{N! h^{3N} Q T} \\ &= k_B \ln(Q) + \frac{\langle \mathcal{H} \rangle}{T} = \frac{-A + \langle \mathcal{H} \rangle}{T}; \\ \Delta S &= \frac{\Delta \langle \mathcal{H} \rangle - \Delta A}{T}. \end{aligned} \quad (2.87)$$

The changes in free energy ΔA are either obtained via the fep scheme or the thermodynamic integration method, and the energy change $\Delta \langle \mathcal{H} \rangle$ can be estimated from the difference in total energy between the two considered states 1 and 2 [35]. Finally, the derivative in Eq. 2.86 could also be evaluated by numerical methods, for instance in terms of the finite difference method, which yields approximate equations of the form [33, 35]

$$\Delta S = - \frac{\Delta A(T + \Delta T) - \Delta A(T - \Delta T)}{2\Delta T}, \quad (2.88)$$

where ΔT is an appropriate temperature interval and $\Delta A(T + \Delta T)$, $\Delta A(T - \Delta T)$ denote the free energy change for the process $1 \rightarrow 2$ at the temperatures $T + \Delta T$ and $T - \Delta T$, respectively. It is clear from Eq. 2.88 that this approach relies on the approximation of a linear dependency between free energy and temperature in the interval $2\Delta T$.

Besides the entropy, thermodynamic response functions as, e.g., heat capacities often yield important contributions to the thermodynamic characterization of a system. In the frame of md simulations, such response functions are most generally expressed as functions of the ensemble averages of fluctuations $\langle \delta O^2 \rangle$ in a mechanical quantity O , which are defined as [32]

$$\langle \delta O^2 \rangle = \langle O^2 \rangle - \langle O \rangle^2. \quad (2.89)$$

In the case of the (N, V, T) ensemble the relevant specific heat capacity is the isochoric heat capacity C_V related to fluctuations in the Hamiltonian according to [32]

$$C_V = \frac{\langle \delta \mathcal{H}^2 \rangle}{k_B T^2}. \quad (2.90)$$

It should be noted that in general estimates of changes in the free energy components ΔH and ΔS via the above sketched approaches are more inaccurate than the calculation of the corresponding free energy change via fep or thermodynamic integration, which is the reason why free energy changes have been discussed in greater detail in this section [33, 36]. Suggestions have been made that a careful sampling protocol (e.g., the consideration of additional sampling stages as in the case of the reasoning behind Eq. 2.79) is of higher importance for accurate estimates of ΔH and ΔS than the actual method of computation [36]. In addition, system specific information might be used to guide the choice of an appropriate computational method, e.g., the calculation of entropy changes in a system near a phase transition via Eq. 2.88 could give rise to problems [33].

2.3.2 A Unified Nonequilibrium Approach

The considerations of the previous part concentrated on two important methods for the computation of free energy changes for a process $1 \rightarrow 2$ on the basis of md simulations, namely free energy perturbation (fep) and thermodynamic integration. These two approaches can be understood as the limiting cases of a more general framework which will be covered in the present section.

The basic idea behind the fep scheme is the sampling of an equilibrium distribution at the initial state 1, from which the *instantaneous* energy differences to the final state 2 are calculated and exponentially weighted, see Eqs. 2.76 and 2.77. From a

formal point of view, there is no sampling of intermediate states or step-by-step changing of the order parameter λ , although the consideration of intermediate stages can considerably contribute to the accuracy of the computed free energy change (compare Eq. 2.79). In contrast, the thermodynamic integration approach relies on the generation of an equilibrium distribution at each individual λ stage, and the free energy change is computed along this equilibrium path from $\lambda = 0$ to $\lambda = 1$ by summing up (integrating) the changes in the Hamiltonian resulting from the variation in λ , see Eqs. 2.83 and 2.84. Along this path, the system is always in equilibrium, which means that the whole process is completely reversible and no dissipation of work into heat takes place. Thus, the work W necessary to initiate (or gained from) the process $1 \rightarrow 2$ directly corresponds to the change in free energy. In a more general framework, one could express the change from $\lambda = 0$ to $\lambda = 1$ as a continuous, time-dependent process, thereby introducing a time dependency in the order parameter $\lambda \rightarrow \lambda(t)$ and thus in the Hamiltonian. If the rate at which λ changes is again very slow, the system will stay in (or near the) equilibrium during the whole process, and the thermodynamic integration formula (see Eq. 2.83) can be rewritten as [37]

$$\Delta A = \lim_{\tau \rightarrow \infty} \int_0^\tau \left. \frac{\partial \mathcal{H}}{\partial \lambda} \right|_{\lambda=\lambda(t)} \dot{\lambda}(t) dt, \quad (2.91)$$

where the dot denotes the rate at which $\lambda(t)$ changes, i.e., the time derivative of λ , and the limit $\tau \rightarrow \infty$ indicates an infinitely slow changing rate, thereby ensuring reversibility. If in contrast the transformation from $\lambda = 0$ to $\lambda = 1$ is done at a *finite* rate, the process will no longer be reversible, since the system will be driven out of equilibrium as the process proceeds. During this irreversible change, the necessary (or gained) work W no longer corresponds to the change in free energy due to the dissipation of work into heat, which implies that on average the performed work is larger than the free energy change

$$\langle W(\tau) \rangle \geq \Delta A, \quad (2.92)$$

where the equality in Eq. 2.92 only holds for the limiting case of a reversible change. Equation 2.92 can be understood as a formulation of the second law of thermodynamics in terms of work and dissipation. Following this reasoning, Eq. 2.91 for finite τ is given as [37]

$$W(\tau) = \int_0^\tau \left. \frac{\partial \mathcal{H}}{\partial \lambda} \right|_{\lambda=\lambda(t)} \dot{\lambda}(t) dt. \quad (2.93)$$

So far, the treatment of a time-dependent change in the order parameter $\lambda(t)$ only led to an inequality between work (which can be obtained from nonequilibrium md simulations) and the change in free energy, see Eq. 2.92. However, Jarzynski demonstrated that the inequality in Eq. 2.92 can be transformed into an equality if instead of W and ΔA the corresponding exponentially weighted quantities are considered [37, 38]

$$\langle \exp(-\beta W(\tau)) \rangle = \exp(-\beta \Delta A). \quad (2.94)$$

Equation 2.94 is widely known as the Jarzynski equality and constitutes a more general framework of the equilibrium concepts which underlie the fep and thermodynamic integration scheme, namely the determination of the free energy change ΔA of a process $1 \rightarrow 2$ for changes in the Hamiltonian (via $\lambda(t)$) at an *arbitrary* rate. There exist several ways for the derivation of Eq. 2.94 (which will not be covered here), of which the relation between the equilibrium Boltzmann distribution and path integral ensemble averages according to the Feynman-Kac theorem is possibly the most instructive and useful variant [37, 39–41].

There are some caveats concerning the practical application of Eq. 2.94 to be considered, though. First of all, the integration of the equations of motion (in case of traditional md simulations) for a time-dependent Hamiltonian can generally lead to larger errors in the trajectories using the conventional integration schemes [32, 37]. Furthermore, the equilibrium distribution for $\lambda = 0$ from which the nonequilibrium trajectories will be generated has to be sampled sufficiently in a way that the different initial configurations are uncorrelated. If this is the case, the corresponding work averages in Eq. 2.94 will also be uncorrelated, thus enabling the application of advanced statistical methods for the free energy estimate like e.g. Bennett’s acceptance ratio approach, which additionally considers the backward direction path (i.e., going from $\lambda = 1$ to $\lambda = 0$) [42, 43]. Such approaches are especially important in the light of the sampling problems discussed for the fep approach in the last section. The comparison of Eqs. 2.94 and 2.78 shows that in both cases the ensemble average is taken over the exponential of a quantity and not over the quantity itself, and as pointed out in the discussion of Eq. 2.78 important contributions to the ensemble average might occur with relatively low probability if both probability distributions do not overlap significantly. In addition, the probability distribution of the work values strongly depends on the transformation path chosen for the process $1 \rightarrow 2$. The occurrence of large barriers which are crossed under tension or a transformation carried out too rapidly without sampling relevant parts of the corresponding phase space can lead to broad work distributions and an increased effect of dissipation [37]. In such cases the obtained free energy change can be subject to a systematical error which will not disappear even if the statistical error is reduced. A possible way to obtain work distributions of smaller width lies in the consideration of additional stages in the overall process $1 \rightarrow 2$ as introduced for the fep methodology in the last section, see Eq. 2.79. However, this approach significantly increases the computational effort, since in order to obtain starting points for the nonequilibrium trajectories a new equilibrium distribution has to be sampled for each new λ stage [37].

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