

Chapter 2

Introduction to Statistical Mechanics

This chapter gives an introduction to the theoretical framework of molecular simulation studies provided by statistical mechanics. Molecular simulations are aimed at predicting macroscopic thermophysical properties based on the behavior of the particles contained in the system. The detailed configuration of the system on the molecular level is called a microstate, and statistical mechanics is the theoretical framework that allows for determining macroscopic properties from studying the properties of the microstate.

Imagine for instance a macroscopic system with rigid and adiabatic walls that contains a constant amount of particles (N), and has a constant volume (V) and internal energy (E). Although these macroscopic properties are fixed, i.e. constrained, we observe a permanent rearrangement of the configuration on the microscopic level as the particles move, exchange energy through collision and redistribute their energies among the different available energy modes (translation, rotation, vibration). Thus, for each macroscopic state there exists a large number of different configurations on the molecular level, the microstates. This collection of microstates that satisfies the fixed properties of the macroscopic system (constraints) is called an ensemble. The choice of constrained properties characterizes different kinds of ensembles that will be discussed in detail in Sect. 2.1.

In molecular simulations, a large number of microstates corresponding to the macroscopic system of interest is generated. In order to perform simulations that are comparable to experimental studies, the simulation ensemble is generally selected in such a way that the constraints correspond to the properties controlled in the experiment. The properties that are not constrained are fluctuating, and predictions for these properties can be provided by analyzing the simulation results by statistical mechanics.

There are two methods to generate a large number of microstates for a given macrostate. In molecular dynamics (MD) simulations, the time evolution of a

microstate is followed by numerically integrating the Newton's equations of motion of its particles with time. The statistical average of a property of interest A is then determined as time average, i.e. from the values $A_i(t)$ of the property at different time steps Δt

$$A_{macro} = \langle A \rangle_{time} = \frac{1}{N_{\Delta t}} \sum_{i=1}^{N_{\Delta t}} A_i(t). \quad (2.1)$$

In Monte Carlo (MC) simulations, different microstates are generated stochastically by elementary changes to the previous configuration. The statistical averages of the thermodynamic properties are then calculated as so called ensemble averages

$$A_{macro} = \langle A \rangle_{ensemble} = \int_{\Gamma} A(\Gamma) \wp(\Gamma) d\Gamma \approx \sum_{\Gamma}^{N_{microstate}} A(\Gamma) \wp(\Gamma) d\Gamma, \quad (2.2)$$

where Γ is the phase space of possible states, and \wp is the probability distribution, i.e. the probability to observe a particular microstate. A basic postulate of statistical mechanics, and therefore of molecular simulation studies, is the “ergodic hypothesis”. It states that ensemble averages are identical with time averages

$$A_{macro} = \langle A \rangle_{time} = \langle A \rangle_{ensemble}, \quad (2.3)$$

i.e. both molecular dynamics and Monte Carlo simulation methods yield the same results for equilibrium properties within the given statistical uncertainties [3]. For the calculation of an ensemble average of a property of interest, the value of this property in a microstate is weighted by the probability that this state occurs. The probability to observe a particular state depends on the constraints imposed on the system. Thus, each kind of ensemble is characterized by its probability distribution or probability density \wp . Another important property of an ensemble is its partition function Q that is the sum of all available states under the given constraints. The partition function contains all the thermodynamic information of the system, i.e. it enables the calculation of all its thermodynamic properties. The partition function therefore is a fundamental quantity for statistical mechanics, comparable to the fundamental equation of state in macroscopic thermodynamics.

Thus, the following Sect. 2.1 will provide an introduction to different kinds of ensembles and the derivations of their probability densities and partition functions. Section 2.2 then connects the partition functions to thermodynamic state variables. Section 2.3 introduces the molecular partition function of the ideal gas as a reference state for simulations on real components. The final section of this chapter deals with the Maxwell-Boltzmann velocity distribution that provides important relations between temperature, velocities and kinetic energy required in MD simulations.

2.1 Ensembles

The concept of ensembles plays a key role in statistical mechanics. As described above, an ensemble is a large number of microstates that all have the same constrained properties as the macroscopic system of interest. Figure 2.1 shows a comparison of the classical ensemble types used in statistical mechanics and the corresponding macroscopic thermodynamic systems.

The microcanonical (NVE) ensemble comprises the collection of microstates that all have the same constant volume V , internal energy E and occupation with N particles. It corresponds to an isolated thermodynamic system with rigid, adiabatic and impermeable walls, which disable the exchange of energy and mass with the environment. The microcanonical ensemble, however, is of little importance for molecular simulation studies on thermophysical properties as the constraints do not correspond to those of real experimental set-ups.

In the canonical (NVT) ensemble, the imposed variables are the volume V , the temperature T , and the number of particles N . Thus, each microstate can be regarded as a closed system with rigid and impermeable walls. Though now the walls are diathermic to allow energy exchange with an isothermal heat bath to ensure constant temperature. This ensemble is used in simulation studies for fluids with known density to predict properties such as pressure, chemical potential, internal energy or transport properties.

The grand canonical (μVT) ensemble is a large number of microstates that all have the same constant volume V and temperature T . Additionally, the chemical potential





ensemble		imposed variables (constraints)	fluctuating properties	corresponding thermodynamic system
microcanonical (NVE)		number of particles N volume V internal energy E	energy (quantum state) of each particle ϵ_i	isolated
canonical (NVT)		number of particles N volume V temperature T	internal energy E_i	closed
grand canonical (μVT)		chemical potential μ volume V temperature T	number of particles N_i internal energy E_i	open
isothermal- isobaric (NPT)		number of particles N pressure p temperature T	volume V_i internal energy E_i	-

Fig. 2.1 Comparison of the classical ensemble types: the constraints properties by which they are characterized and the properties that fluctuate. Also given is the macroscopic thermodynamic system type it can be compared with

μ is imposed, whereas the amount of particles in the system can fluctuate. The grand canonical ensemble corresponds to an open system with rigid but diathermic and permeable walls that enable both mass and energy exchange with the environment. The grand canonical ensemble is the only ensemble in which the number of particles in the system is not an imposed variable. It is therefore used in molecular simulation studies on adsorption or chemical reactions.

The imposed variables of the isothermal-isobaric (NpT) ensemble are pressure p , temperature T and the amount of particles N . Although it does not correspond to a classical thermodynamic system, the NpT ensemble is widely used in molecular simulation studies as its constraints match usual experimental conditions. Simulations in the NpT ensemble therefore enable the prediction of thermophysical properties as a function of temperature and pressure in comparison with experimental results.

Following this short introduction to the classical ensemble types and their application in molecular simulation studies, the next sections provide more details on their theoretical description in statistical mechanics and the derivation of their probability density and partition function. A more detailed description is provided for instance in the textbooks by Van Carey [9], Hill [4], Weingärtner [10], Sears and Salinger [8] or Gasser and Richards [2].

2.1.1 The Microcanonical Ensemble

The microcanonical ensemble can be visualized as n copies of an isolated system that all have the same volume V , internal energy E and constant number of particles N , as shown in Fig. 2.2.

Although the total internal energy of the system E is constant, it is continuously redistributed between the particles, so that the energy of each particle ε_i —or its quantum state—fluctuates. When N_i is the number of particles that occupy the quantum state i with the energy level ε_i , the total energy of the system is given by

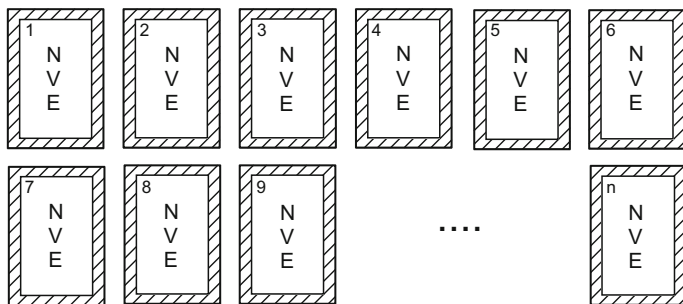


Fig. 2.2 Depiction of the microcanonical (NVE) ensemble: n copies of an isolated system with constant volume V and internal energy E , consisting of N equal particles

$$E = \sum_i \varepsilon_i N_i \quad (2.4)$$

The given constraint that the total energy has to be constant yields

$$dE = \sum_i \varepsilon_i dN_i = 0. \quad (2.5)$$

Additionally, the total number of particles is constant, i.e.

$$N = \sum_i N_i = \text{const.} \quad \text{and} \quad dN = \sum_i dN_i = 0. \quad (2.6)$$

However, for a given number of particles N and total energy E , a number of possibilities still exist to distribute the particles on the different available quantum states ε_i , i.e. different distribution functions N_1, N_2, \dots, N_i . Figure 2.3 exemplarily shows some feasible distributions of $N = 8$ particles on four different quantum states $\varepsilon_0, \varepsilon_1, \varepsilon_2, \varepsilon_3$ for a constraint total energy of $E = 16 \text{ meV}$. Provided that the different particles are distinguishable (in the example of Fig. 2.3 by the numbering), a number of possibilities (microstates) exist to realize a specific distribution. The number of different microstates for a given distribution can be obtained from combinatorial analysis

$$W_{NVE} = \frac{N!}{\prod_{i=0}^{\infty} N_i!}. \quad (2.7)$$

W is called the thermodynamic probability and gives the total number of microstates consistent with the given distribution—it can therefore be regarded as degree of disorder of the system. As exemplification, Fig. 2.3 also provides the thermodynamic probabilities W of the given distributions. The most famous equation in statistical mechanics is Boltzmann's entropy hypothesis

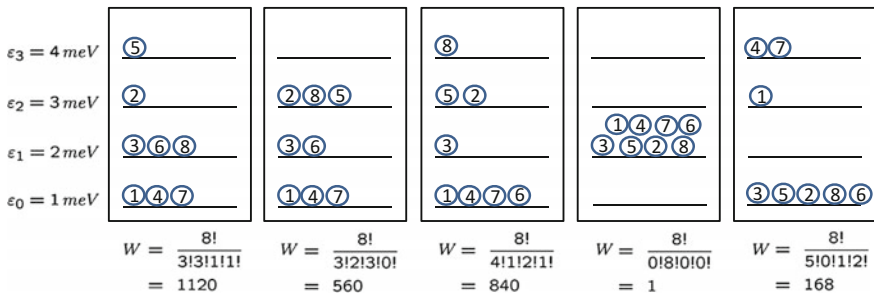


Fig. 2.3 Example for different potential distributions of $N = 8 = \text{const.}$ particles on four quantum states $\varepsilon_0 = 1 \text{ meV}, \varepsilon_1 = 2 \text{ meV}, \varepsilon_2 = 3 \text{ meV}, \varepsilon_3 = 4 \text{ meV}$ for a constrained total energy of $E = 16 \text{ meV}$. Also given is the number of different ways W to realize a particular distribution for distinguishable particles, employing Eq. 2.7

$$S = k_B \ln(W_{NVE}) \quad (2.8)$$

that relates the entropy to the logarithm of the thermodynamic probability W , and with this links statistical mechanics to classical thermodynamics.

Thus, the equilibrium state is the state with maximum entropy and according to Eq. 2.8, the state with the highest probability, i.e. the distribution with the highest number of different microstates. The condition of equilibrium can be formulated as

$$S \rightarrow \max, \quad W_{NVE} \rightarrow \max, \quad \ln(W_{NVE}) \rightarrow \max. \quad (2.9)$$

$$\Rightarrow d(\ln(W_{NVE})) = 0 \rightarrow dS = 0. \quad (2.10)$$

Applying the Sterling formula

$$\ln x! = x \cdot \ln x - x$$

yields

$$\ln(W_{NVE}) = \ln(N!) - \sum_{i=0}^{\infty} \ln(N_i!) \quad (2.11)$$

$$= - \sum_{i=0}^{\infty} N_i \ln \left(\frac{N_i}{N} \right). \quad (2.12)$$

When determining the most probable distribution by minimizing Eq. 2.11, the existing constraints of the ensemble have to be taken into account. This is usually done by employing Lagrange's method of undetermined multipliers [7], i.e. by multiplying the differentials of the equations of constraint in Eqs. 2.5 and 2.6 with Lagrangian multipliers β and α to incorporate them into Eq. 2.11. Thus, the resulting equation to be solved is

$$\sum_{i=0}^{\infty} \left[\ln \left(\frac{N_i}{N} \right) + \alpha + \beta \varepsilon_i \right] dN_i = 0 \quad \Rightarrow \quad \frac{N_i}{N} = e^{-\alpha} e^{-\beta \varepsilon_i}. \quad (2.13)$$

The multiplier α results from the condition

$$\sum_{i=0}^{\infty} \frac{N_i}{N} = 1 \quad \Rightarrow \quad e^{-\alpha} = \frac{1}{\sum_{i=0}^{\infty} e^{-\beta \varepsilon_i}}. \quad (2.14)$$

Thus, the probability density \wp_{NVE} of the microcanonical ensemble is then given by

$$\wp_{NVE} = \frac{N_i}{N} = \frac{e^{-\beta \varepsilon_i}}{\sum_{j=0}^{\infty} e^{-\beta \varepsilon_j}} \quad \text{with} \quad \beta = \frac{1}{k_B T}, \quad (2.15)$$

and expresses the probability that particles occupy the quantum state i with an energy level ε_i . The denominator in Eq. 2.15 is the so called molecular partition function q

$$q = \sum_{j=0}^{\infty} e^{-\beta \varepsilon_j}, \quad (2.16)$$

and is the sum of all available energy levels (quantum states) of the particles. When the energy levels ε_i are g_i times degenerated, Eq. 2.16 can also be expressed by

$$q = \sum_{\text{energy levels } i} g_i e^{-\beta \varepsilon_i}. \quad (2.17)$$

The molecular partition function q has to be distinguished from the partition function Q_{NVE} of the microcanonical ensemble. Q_{NVE} gives the number of accessible state associated with the system energy E at given constant values of N and V . It can be written as [1]

$$Q_{NVE} = \sum_{\Gamma} \delta_i(E_i - E) \quad \text{with} \quad (2.18)$$

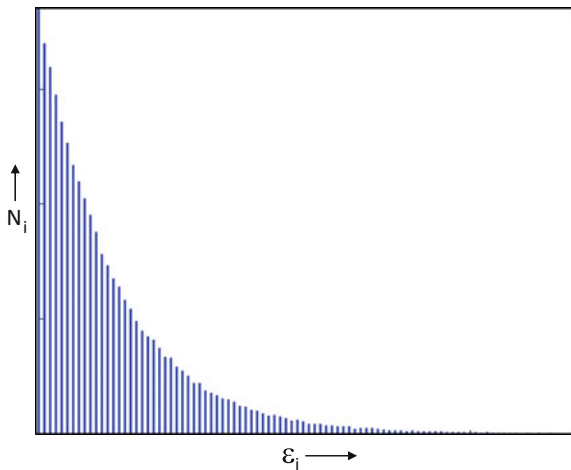
$$\delta_i(E_i - E) = 1, \quad \text{for } E - \Delta E \leq E_i < E$$

$$\delta_i(E_i - E) = 0, \quad \text{else.}$$

Therein δ_i is the Kronecker delta, and Δ the uncertainty with which the energy E can be determined [4].

The term $\exp(-\beta \varepsilon_i)$ in Eq. 2.16 is the so called Boltzmann factor. The resulting distribution of the particles among the different energy levels (quantum states) ε_i ,

Fig. 2.4 Boltzmann distribution as most probable distribution of $N = \text{const.}$ particles on different energy levels for a constrained total energy $E = \text{const}$



is the Boltzmann distribution shown in Fig. 2.4 that represents the most probable distribution of a thermodynamic system with $N, E = \text{const.}$

2.1.2 The Canonical Ensemble

The canonical ensemble represents n copies of a closed system that all have the same volume V , temperature T and constant number of particles N . All copies are in thermal contact by being arranged in a large isothermal heat bath. Thus, the energy E_i of each copy, i.e. ensemble member, may fluctuate. However, the entire collection of the n copies is adiabatic, as shown in Fig. 2.5.

When n_i stands for the number of ensemble members with the same energy E_i , the total energy of the system is given by

$$U = \sum_i n_i E_i. \quad (2.19)$$

As the total system is thermally isolated with regard to the environment, its total energy U has to be constant, which yields the constraint

$$dU = \sum_i E_i dn_i = 0. \quad (2.20)$$

Additionally, the total number n of ensemble members is constant that gives the constraints

$$n = \sum_i n_i = \text{const.} \quad \text{and} \quad dn = \sum_i dn_i = 0. \quad (2.21)$$

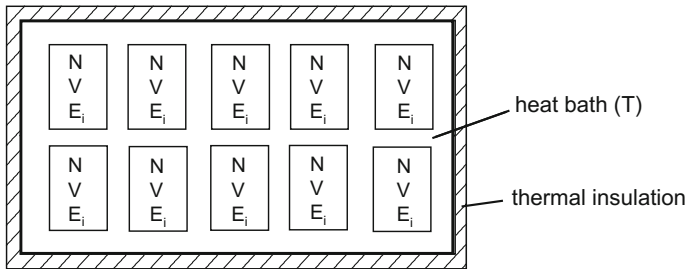


Fig. 2.5 Depiction of the canonical (NVT) ensemble: n copies of a closed system with constant volume V and fixed temperature T , consisting of N equal particles. The internal energy E_i of each copy fluctuates

A particular distribution is characterized by the n_1, n_2, \dots, n_i , i.e. number of ensemble members n_i residing in a microstate i with the energy E_i . For the NVT ensemble, the number of ways to obtain a specific distribution is given by

$$W_{NVT} = \frac{n!}{\prod_{i=0}^{\infty} n_i!}. \quad (2.22)$$

Again, the equilibrium distribution is the most probable distribution realized by the maximum number of different microstates. It is determined by maximizing Eq. 2.22 and employing the Lagrange's method of undetermined multipliers to consider the constraints of the ensemble. When the multiplier for the energy constraint in Eq. 2.20 is $\beta = 1/(k_B T)$, the resulting equation to be solved is

$$\sum_{i=0}^{\infty} \left[\ln \left(\frac{n_i}{n} \right) + \alpha + \frac{E_i}{k_B T} \right] dn_i = 0 \quad \Rightarrow \quad \frac{n_i}{n} = e^{-\alpha} e^{-E_i/k_B T} \quad (2.23)$$

The undetermined multiply α is derived from

$$\sum_{i=0}^{\infty} \frac{n_i}{n} = 1 \quad \Rightarrow \quad e^{-\alpha} = \frac{1}{\sum_{i=0}^{\infty} e^{-E_i/k_B T}} \quad (2.24)$$

Thus, the probability that an ensemble member has the energy E_j is given by

$$\wp_{NVT} = \frac{n_j}{n} = \frac{e^{-E_j/k_B T}}{\sum_{i=0}^{\infty} e^{-E_i/k_B T}} \quad (2.25)$$

with the denominator in Eq. 2.25 being the partition function Q_{NVT} of the canonical ensemble

$$Q_{NVT} = \sum_{i=0}^{\infty} e^{-E_i/k_B T}. \quad (2.26)$$

Combining all energy states belonging to the same system energy level E_j , Q_{NVT} can also be expressed by

$$Q_{NVT} = \sum_{\text{levels } E_j} Q_{NVE}(E_j, V, N) e^{-E_j/k_B T}, \quad (2.27)$$

wherein the microcanonical partition function $Q_{NVE}(E_j, V, N)$ gives the number of states with the energy E_j . The canonical partition function Q_{NVT} is related to the molecular partition function q by

$$Q_{NVT} = q^N \quad \text{for } N \text{ distinguishable particles} \quad (2.28)$$

$$Q_{NVT} = \frac{q^N}{N!} \quad \text{for } N \text{ indistinguishable particles,} \quad (2.29)$$

where for instance particles of an ideal gas are indistinguishable, whereas particles in a solid crystal are distinguishable by their coordinates in the lattice. Equation (2.26) gives the canonical partition function over all quantum states of the system, whereas molecular simulations require the formulation of the Q_{NVT} in the classical phase space Γ . In the classical formulation, the total energy E_i is divided into the kinetic energy E_{kin} and the potential, i.e. configurational energy U_{conf} that arises from interactions between the particles. Thus, the phase space is defined by the positions r and momenta p of the N particles within the system. However, according to the uncertainty principle in quantum mechanics, a state in phase space, defined by $dr dp$, can only be located with an uncertainty of h , the Planck's constant [4]. Taking this into account, a state in the phase space $d\Gamma$ in a 3-dimensional system with N undistinguishable particles is given by

$$d\Gamma = \frac{1}{N!} \frac{1}{h^{3N}} dr^{3N} dp^{3N}. \quad (2.30)$$

As the energy levels are quite close together compared to $k_B T$, the sum over all energy states can be approximated by an integral, so that finally the classical formulation of the canonical partition function is given by [1]

$$Q_{NVT} = \frac{1}{N!} \frac{1}{h^{3N}} \int \int e^{-E_i/k_B T} dr^{3N} dp^{3N}. \quad (2.31)$$

2.1.3 The Grand Canonical Ensemble

Similar to the canonical ensemble, the grand canonical ensemble can be visualized by n copies of a system that all have the same volume V , and that are immersed in a large isothermal heat bath so that all members have the same temperature T . But now, the walls of the copies are permeable to allow crossing over of particles from one copy to another. Thus, both the energy E_i and the number of particles N_j in each member of the ensemble fluctuate. Again, the entire collection of the n copies is isolated from the environment so that its total energy U and total number of particles N remain constant. A depiction of the grand canonical ensemble is shown in Fig. 2.6.

When n_{N_j, E_i} is the number of copies that consist of a particular amount of particles N_j and have an energy of E_i , the constraints of the grand canonical ensemble can be expressed by

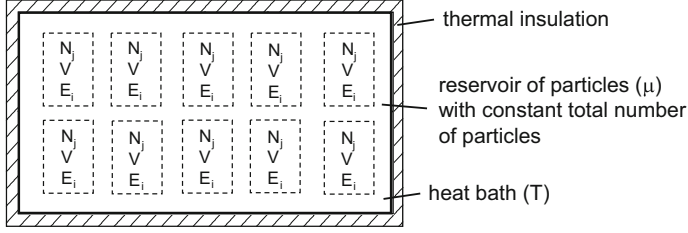


Fig. 2.6 Depiction of the grand canonical (μVT) ensemble: n copies of an open system with constant volume V and fixed temperature T and chemical potential μ . The occupation N_j and the internal energy E_i fluctuate

$$\begin{aligned}
 \sum_{N_j=0}^{\infty} \sum_{i=0}^{\infty} n_{N_j, E_i} &= n = \text{const.} \quad \Rightarrow \quad dn = \sum_{N_j=0}^{\infty} \sum_{i=0}^{\infty} dn_{N_j, E_i} = 0 \\
 \sum_{N_j=0}^{\infty} \sum_{i=0}^{\infty} E_i n_{N_j, E_i} &= U = \text{const.} \quad \Rightarrow \quad dU = \sum_{N_j=0}^{\infty} \sum_{i=0}^{\infty} E_i dn_{N_j, E_i} = 0 \\
 \sum_{N_j=0}^{\infty} \sum_{i=0}^{\infty} N_j n_{N_j, E_i} &= N = \text{const.} \quad \Rightarrow \quad dN = \sum_{N_j=0}^{\infty} \sum_{i=0}^{\infty} N_j dn_{N_j, E_i} = 0
 \end{aligned}$$

The number of ways to realize a particular distribution n_{N_j, E_i} is given by

$$W_{\mu VT} = \frac{n!}{\prod_{N_j=0}^{\infty} \prod_{i=0}^{\infty} n_{N_j, E_i}!}. \quad (2.32)$$

The state of thermodynamic equilibrium, i.e. state with the highest probability is determined from solving $d \ln W_{\mu VT} = 0$ subject to the constraints expressed above. This yields

$$\sum_{N_j=0}^{\infty} \sum_{i=0}^{\infty} \left[\ln \frac{n_{N_j, E_i}}{n} + \alpha + \frac{E_i}{k_B T} + b N_j \right] dn_{N_j, E_i} = 0 \quad (2.33)$$

$$\Rightarrow \quad \frac{n_{N_j, E_i}}{n} = e^{-\alpha} e^{-\frac{E_i}{k_B T} - b N_j} \quad (2.34)$$

Again, the multiplier α is derived from the condition

$$\sum_{N_j=0}^{\infty} \sum_{i=0}^{\infty} \frac{n_{N_j, E_i}}{n} = 1 \quad (2.35)$$

Thus, the probability of finding an ensemble member with the energy E_i and the number of particles N_j is

$$\mathcal{Q}_{\mu VT} = \frac{n_{N_j, E_j}}{n} = \frac{e^{(-E_i/k_B T - b N_j)}}{\sum_{N_j=0}^{\infty} \sum_{i=0}^{\infty} e^{(-E_i/k_B T - b N_j)}} \quad (2.36)$$

where the denominator represents the partition function $Q_{\mu VT}$ of the grand canonical ensemble. The multiplier b can be determined from

$$dS = k_B d(\ln W_{\mu VT}) = -k_B \sum_{N_j=0}^{\infty} \sum_{i=0}^{\infty} \ln(n_{N_j, E_i}) dn_{N_j, E_i} \quad (2.37)$$

$$= \frac{1}{T} \underbrace{\sum_{N_j=0}^{\infty} \sum_{i=0}^{\infty} E_i dn_{N_j, E_i}}_{dU} + k_B b \underbrace{\sum_{N_j=0}^{\infty} \sum_{i=0}^{\infty} N_j dn_{N_j, E_i}}_{dN} \quad (2.38)$$

The first double summation in Eq. 2.38 represents the change in the total internal energy dU , whereas the second summation specifies the change in the total number of particles dN . Thus, a comparison with the Gibbs fundamental equation of state for $dV = 0$ yields the relation of the multiplier b and the chemical potential μ

$$-\frac{\mu}{T} = k_B b \quad \Rightarrow \quad b = \frac{-\mu}{k_B T}. \quad (2.39)$$

With this, the partition function of the grand canonical ensemble becomes

$$Q_{\mu VT} = \sum_{N_j=0}^{\infty} \sum_{i=0}^{\infty} e^{\frac{-(E_i - \mu N_j)}{k_B T}} \quad (2.40)$$

In the classical formulation, the partition function of the grand canonical ensemble of N indistinguishable particles is given by [1]

$$Q_{\mu VT} = \sum_N \frac{1}{N!} \frac{1}{h^{3N}} e^{\frac{\mu N}{k_B T}} \int \int e^{-E_i/k_B T} dr^{3N} dp^{3N} = \sum_N \left(e^{\frac{\mu N}{k_B T}} Q_{NVT} \right). \quad (2.41)$$

2.1.4 The NpT -Ensemble

The NpT ensemble represents n copies of a closed system with the same constant number of particles N . The members of the ensemble are arranged in a large isothermal heat bath and pressure chamber to ensure that they all have the same temperature and pressure, whereas their energy E_i and volume V_j fluctuate. However, the entire collection of the n copies is adiabatic and has a constant total volume V , as shown in Fig. 2.7.

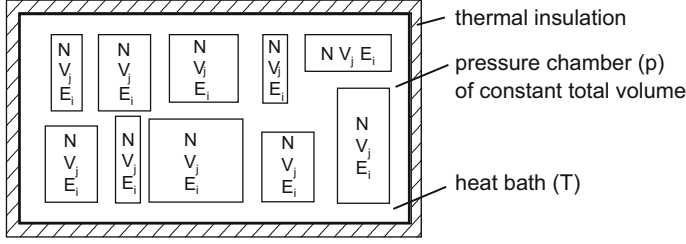


Fig. 2.7 Depiction of the NpT ensemble: n copies of a system with fixed temperature T and pressure p , consisting of N equal particles. The volume V_i and internal energy E_i of each copy fluctuate

For the NpT -Ensemble, n_{V_j, E_i} is the number of copies with a particular volume V_j and energy E_i . The constraints of the ensemble are given by

$$\begin{aligned} \sum_{V_j=0}^{\infty} \sum_{i=0}^{\infty} n_{V_j, E_i} &= n = \text{const.} \Rightarrow dn = \sum_{V_j=0}^{\infty} \sum_{i=0}^{\infty} dn_{V_j, E_i} = 0 \\ \sum_{V_j=0}^{\infty} \sum_{i=0}^{\infty} E_i n_{V_j, E_i} &= U = \text{const.} \Rightarrow dU = \sum_{V_j=0}^{\infty} \sum_{i=0}^{\infty} E_i dn_{V_j, E_i} = 0 \\ \sum_{V_j=0}^{\infty} \sum_{i=0}^{\infty} V_j n_{V_j, E_i} &= V = \text{const.} \Rightarrow dV = \sum_{V_j=0}^{\infty} \sum_{i=0}^{\infty} V_j dn_{V_j, E_i} = 0 \end{aligned}$$

The thermodynamic probability W_{NpT} gives the number of possibilities to realize a specific distribution n_{V_j, E_i} , and can again be derived from combinatorial analysis. This yields

$$W_{NpT} = \frac{n!}{\prod_{V_j=0}^{\infty} \prod_{i=0}^{\infty} n_{V_j, E_i}!}. \quad (2.42)$$

Thus, the most probable distribution subject to the constraints of the NpT ensemble can be determined from solving

$$\sum_{V_j=0}^{\infty} \sum_{i=0}^{\infty} \left[\ln \frac{n_{V_j, E_i}}{n} + \alpha + \frac{E_i}{k_B T} + b V_j \right] dn_{V_j, E_i} = 0 \quad (2.43)$$

$$\Rightarrow \frac{n_{V_j, E_i}}{n} = e^{-\alpha} e^{\left(-\frac{E_i}{k_B T} - b V_j \right)}. \quad (2.44)$$

With the multiplier α derived from the condition

$$\sum_{V_j=0}^{\infty} \sum_{i=0}^{\infty} \frac{n_{V_j, E_i}}{n} = 1, \quad (2.45)$$

the probability \wp_{NpT} that a microstate has a particular combination of energy E_i and volume V_j is

$$\wp_{NpT} = \frac{n_{V_j, E_i}}{n} = \frac{e^{(-E_i/k_B T - b V_j)}}{\sum_{V_j=0}^{\infty} \sum_{i=0}^{\infty} e^{(-E_i/k_B T - b V_j)}}. \quad (2.46)$$

The multiplier b can be determined by comparing the expression for dS of the NpT ensemble

$$dS = k_B d(\ln W_{NpT}) = -k_B \sum_{V_j=0}^{\infty} \sum_{i=0}^{\infty} \ln(n_{V_j, E_i}) dn_{V_j, E_i} \quad (2.47)$$

$$= \frac{1}{T} \sum_{V_j=0}^{\infty} \sum_{i=0}^{\infty} E_i dn_{V_j, E_i} + k_B b \sum_{V_j=0}^{\infty} \sum_{i=0}^{\infty} V_j dn_{V_j, E_i} \quad (2.48)$$

with the Gibbs fundamental equation of state for $dN = 0$. This yields

$$k_B b \sum_{V_j=0}^{\infty} \sum_{i=0}^{\infty} V_j dn_{V_j, E_i} = k_B b dV = \frac{p}{T} dV \quad \Rightarrow \quad b = \frac{p}{k_B T} \quad (2.49)$$

Thus, the partition function of the NpT ensemble, which is given by the dominator in Eq. 2.46, is

$$Q_{NpT} = \sum_{V_j=0}^{\infty} \sum_{i=0}^{\infty} e^{\frac{-(E_i + p V_j)}{k_B T}} \quad (2.50)$$

In the classical formulation, the partition function of the NpT ensemble of N indistinguishable particles is [1]

$$Q_{NpT} = \frac{1}{N!} \frac{1}{h^{3N}} \frac{1}{V_0} \int e^{-p V_j / k_B T} dV \int \int e^{-E_i / k_B T} dr^{3N} dp^{3N} \quad (2.51)$$

$$= \frac{1}{V_0} \int Q_{NVT} e^{-p V_j / k_B T} dV, \quad (2.52)$$

wherein the basic unit of volume V_0 is included to render Q_{NpT} dimensionless. Another common choice for the volume scale is the factor βp instead of V_0^{-1} .

2.2 Thermodynamic Properties of the Ensemble

As described above, the partition function in statistical thermodynamics is of similar importance as the fundamental equation of state in macroscopic thermodynamics. From the partition function, all thermodynamic properties of the ensemble can be obtained from derivatives or by algebraic operations. The connection of the partition function to thermodynamics is established by the bridge equation [6]

$$\Psi_{ensemble} = -\ln Q_{ensemble}, \quad (2.53)$$

where Ψ is the thermodynamic potential of the ensemble, i.e. the property whose minimum defines the equilibrium condition—in accordance with the thermodynamic potentials in macroscopic thermodynamics. The definitions of thermodynamic potentials of macrostates and microstates are compared in Table 2.1.

Thus, the thermodynamic properties of the **microcanonical ensemble** can be derived from the bridge equation

$$S = k_B \ln Q_{NVE}. \quad (2.54)$$

A comparison with the Gibbs Fundamental equation of state for the entropy S

$$dS = \frac{1}{T}dE + \frac{p}{T}dV - \frac{\mu}{T}dN. \quad (2.55)$$

yields the relation between the molecular partition function Q_{NVE} and the thermodynamic properties T , p and μ

$$\frac{1}{T} = \left(\frac{\partial S}{\partial E} \right)_{V,N} = k_B \left(\frac{\partial \ln Q_{NVE}}{\partial E} \right)_{V,N} \quad (2.56)$$

$$\frac{p}{T} = \left(\frac{\partial S}{\partial V} \right)_{E,N} = k_B \left(\frac{\partial \ln Q_{NVE}}{\partial V} \right)_{E,N} \quad (2.57)$$

Table 2.1 Comparison of thermodynamic potentials in macroscopic and statistical thermodynamics [6]

Macrostate		Microstate	
System	Thermodynamic potential	Ensemble	$\Psi_{ensemble}$
$U, V, n = \text{const.}$	Entropy: $-S \rightarrow \min.$	Microcanonical	$\Psi_{NVE} = -\frac{S}{k_B}$
$T, V, n = \text{const.}$	Helmholtz: $F \rightarrow \min.$	Canonical	$\Psi_{NVT} = -\frac{F}{k_B T}$
$T, p, n = \text{const.}$	Gibbs: $G \rightarrow \min.$	NpT	$\Psi_{NpT} = -\frac{G}{k_B T}$
$\mu, V, T = \text{const.}$	Hill: $-pV \rightarrow \min.$	Grand canonical	$\Psi_{\mu VT} = -\frac{pV}{k_B T}$

$$\frac{\mu}{T} = - \left(\frac{\partial S}{\partial N} \right)_{E,V} = -k_B \left(\frac{\partial \ln Q_{NVE}}{\partial N} \right)_{E,V}. \quad (2.58)$$

In a similar way, the correlations between the thermodynamic properties S , p , μ and U and the partition function Q_{NVT} of the **canonical ensemble** can be derived from the bridge equation

$$F = -k_B T \ln Q_{NVT}, \quad (2.59)$$

and the formulation of the Gibbs Fundamental equation of state for the Helmholtz energy F

$$dF = -SdT - pdV + \mu dN. \quad (2.60)$$

This yields

$$S = - \left(\frac{\partial F}{\partial T} \right)_{V,N} = k_B \left(\ln Q_{NVT} + T \left(\frac{\partial \ln Q_{NVT}}{\partial T} \right)_{V,N} \right) \quad (2.61)$$

$$p = - \left(\frac{\partial F}{\partial V} \right)_{T,N} = k_B T \left(\frac{\partial \ln Q_{NVT}}{\partial V} \right)_{T,N} \quad (2.62)$$

$$\mu = \left(\frac{\partial F}{\partial N} \right)_{T,V} = -k_B T \left(\frac{\partial \ln Q_{NVT}}{\partial N} \right)_{T,V} \quad (2.63)$$

$$U = F + TS = k_B T^2 \left(\frac{\partial \ln Q_{NVT}}{\partial T} \right)_{V,N} \quad (2.64)$$

For the **NpT ensemble** the bridge equation becomes

$$G = -k_B T \ln Q_{NpT}. \quad (2.65)$$

By means of the Gibbs Fundamental equation of state for the Gibbs energy G

$$dG = -SdT + Vdp + \mu dN, \quad (2.66)$$

the thermodynamic properties S , V , μ and H can be related to the partition function Q_{NpT} by

$$S = - \left(\frac{\partial G}{\partial T} \right)_{p,N} = k_B \left(\ln Q_{NpT} + T \left(\frac{\partial \ln Q_{NpT}}{\partial T} \right)_{p,N} \right) \quad (2.67)$$

$$V = \left(\frac{\partial G}{\partial p} \right)_{T,N} = -k_B T \left(\frac{\partial \ln Q_{NpT}}{\partial p} \right)_{T,N} \quad (2.68)$$

$$\mu = \left(\frac{\partial G}{\partial N} \right)_{p,T} = -k_B T \left(\frac{\partial \ln Q_{NpT}}{\partial N} \right)_{p,T} \quad (2.69)$$

$$H = G + TS = k_B T^2 \left(\frac{\partial \ln Q_{NpT}}{\partial T} \right)_{p,N} \quad (2.70)$$

Finally, the bridge equation of the **grand canonical ensemble** is given by

$$pV = k_B T \ln Q_{\mu VT}. \quad (2.71)$$

The differential of the Euler equation in consideration of the Gibbs Fundamental equation of state yields

$$d(pV) = SdT + pdV + Nd\mu. \quad (2.72)$$

Thus, the thermodynamic properties S , p and N can be derived from the partition function $Q_{\mu VT}$ by

$$S = \left(\frac{\partial(pV)}{\partial T} \right)_{V,\mu} = k_B \left(\ln Q_{\mu VT} + T \left(\frac{\partial \ln Q_{\mu VT}}{\partial T} \right)_{V,\mu} \right) \quad (2.73)$$

$$p = \left(\frac{\partial(pV)}{\partial V} \right)_{T,\mu} = k_B T \left(\frac{\partial \ln Q_{\mu VT}}{\partial V} \right)_{T,\mu} \quad (2.74)$$

$$N = \left(\frac{\partial(pV)}{\partial \mu} \right)_{V,T} = k_B T \left(\frac{\partial \ln Q_{\mu VT}}{\partial \mu} \right)_{V,T}. \quad (2.75)$$

In general, those properties that are derived from derivatives of the partition functions, i.e. the pressure p , volume V , the energy U and the enthalpy H are referred to as mechanical properties. These properties are easily evaluated in molecular simulations studies. However, the properties Gibbs energy G , the free or Helmholtz energy F , or the entropy S itself are related to the partition function directly and are so called statistical quantities. Thus, special simulation techniques are required (see Sect. 7.4) to obtain acceptable estimates for the entropy related properties.

2.3 Molecular Partition Function of the Ideal Gas

The partition function contains all the thermodynamic information of the system, and its knowledge allows for the calculation of all thermodynamic functions. However, the same problems that exist for setting up a physical based fundamental equation of state for a real compound also arise for formulating its partition function. The physics of real systems are too complex and are still not completely understood so that it is impossible to find a physical and mathematical consistent description of all the energy levels of a compound that is necessary to formulate its partition function. Thus, the exact formulation of a partition function is limited to simple and idealized systems such as the ideal gas, for which the energy levels are known accurately and for which

it can be assumed that the system's energy is the sum of energies of its particles [2]. As the total energy of an ideal gas can be divided into independent contributions from translational, rotational, vibrational motions and from the electronic and nuclear energy levels, the total molecular partition functions can be expressed as

$$q = q^{trans} \cdot q^{rot} \cdot q^{vib} \cdot q^{elec} \cdot q^{nucl}. \quad (2.76)$$

Thus, the following subsections will provide an overview over the different contributions to the partition function for an ideal gas.

2.3.1 Partition Function of Translational Motion

The translational partition function can be derived by considering N monoatomic molecules of an ideal gas. Each atom is treated as mass point of mass m and the gas is enclosed in a cubic container of volume V and side length L . The energy level ε_i^{trans} of an atom is its kinetic energy associated with its translational motion in the three directions in space

$$\varepsilon_i^{trans} = \frac{p_x^2 + p_y^2 + p_z^2}{2m}. \quad (2.77)$$

In quantum mechanics, the so called de Broglie relation states that the wavelength λ of an atom is Planck's constant h divided by the atom's momentum

$$\lambda = \frac{h}{p}. \quad (2.78)$$

The wavelength in turn is related to the container's side length L , as a multiplier of half the wavelength has to fit into the box [2]. Thus,

$$\lambda = \frac{2L}{n}, \quad (2.79)$$

with the quantum number n . Therefore, according to the de Broglie relation, the momentum for each dimensional coordinate can be expressed as

$$p_x = \frac{hn_x}{2L_x}, \quad p_y = \frac{hn_y}{2L_y}, \quad p_z = \frac{hn_z}{2L_z}, \quad (2.80)$$

and hence the kinetic energy level as

$$\varepsilon_i^{trans} = \frac{h^2}{8m} \left(\frac{n_x^2}{L_x^2} + \frac{n_y^2}{L_y^2} + \frac{n_z^2}{L_z^2} \right). \quad (2.81)$$

The molecular partition function of the translational motion then becomes

$$\begin{aligned}
 q^{trans} &= \sum_{i=0}^{\infty} e^{-\frac{\varepsilon_i^{trans}}{k_B T}} \\
 &= \left(\sum_{i=1}^{\infty} e^{-\frac{h^2}{8mk_B T} \left(\frac{n_x}{L_x}\right)^2} \right) \cdot \left(\sum_{i=1}^{\infty} e^{-\frac{h^2}{8mk_B T} \left(\frac{n_y}{L_y}\right)^2} \right) \cdot \left(\sum_{i=1}^{\infty} e^{-\frac{h^2}{8mk_B T} \left(\frac{n_z}{L_z}\right)^2} \right) \\
 &= q_x^{trans} \cdot q_y^{trans} \cdot q_z^{trans}.
 \end{aligned} \tag{2.82}$$

As the energy levels ε_i^{trans} are in general very close together, the sums can be approximated by integrals. Thus, the molecular partition function for the x -dimension for instance can be written as

$$\begin{aligned}
 q_x^{trans} &= \sum_{i=1}^{\infty} e^{-\frac{h^2}{8mk_B T} \left(\frac{n_x}{L_x}\right)^2} \approx \int_0^{\infty} e^{-\frac{h^2}{8mk_B T} \left(\frac{n_x}{L_x}\right)^2} dn_x \\
 &= \frac{L_x}{2} \sqrt{\frac{8\pi mk_B T}{h^2}}
 \end{aligned} \tag{2.83}$$

The product of the three side lengths $L_x L_y L_z$ gives the container volume V . Therefore, the total translational partition function as product of the partition functions for the three dimensions becomes

$$q^{trans} = V \left(\sqrt{\frac{2\pi mk_B T}{h^2}} \right)^3 = \frac{V}{\Lambda^3} \tag{2.84}$$

where Λ is the de Broglie wavelength

$$\Lambda = \sqrt{\frac{h^2}{2\pi mk_B T}}. \tag{2.85}$$

According to Eq. 2.28, the canonical partition function of translational motion for a system of N indistinguishable particles then becomes

$$Q_{NVT}^{trans} = \frac{(q^{trans})^N}{N!} = \frac{V^N}{\Lambda^{3N} N!}. \tag{2.86}$$

As we will see that the canonical partition function of translational motion is the only volume dependent contribution to the partition function of the ideal gas, we can derive from Eq. 2.86 an expression for the pressure of the ideal gas, by employing the relation given by Eq. 2.62. With the Sterling equation $\ln(x!) = x \ln x - x$, we can express

$$\ln Q_{NVT}^{trans} = N \ln V - 3N \ln \Lambda - (N \ln N - N) \quad (2.87)$$

Thus, Eq. 2.62 yields

$$p^{id} = k_B T \left(\frac{\partial \ln Q_{NVT}^{trans}}{\partial V} \right)_{T,N} = k_B T \frac{N}{V}, \quad (2.88)$$

i.e. the well known ideal gas law. Accordingly, the chemical potential of the monoatomic ideal gas can be derived from Eq. 2.63

$$\mu^{id} = -k_B T \left(\frac{\partial \ln Q_{NVT}^{trans}}{\partial N} \right)_{T,V} = -k_B T \ln \left(\frac{V}{N \Lambda^3} \right) \quad (2.89)$$

2.3.2 Partition Function of Rotational Motion

The energy level ε_i^{rot} of a polyatomic molecule associated with its rotational motion can be subdivided into motions around the three axes x, y, z with the three moments of inertia I_{xx}, I_{yy}, I_{zz}

$$\varepsilon_i^{rot} = \frac{j_x^2}{2I_{xx}} + \frac{j_y^2}{2I_{yy}} + \frac{j_z^2}{2I_{zz}} \quad (2.90)$$

where j_x, j_y, j_z are the three angular momenta.

In case of a linear diatomic molecule for which z is the axis of symmetry, the moment of inertia I_{zz} is too small so that it only has two rotational degrees of freedom. When the diatomic molecule is regarded as rigid and symmetric rotor (dumbball) with $I_{xx} = I_{yy} = I$ and $j_x = j_y = j$, the classical kinetic energy of rotation becomes

$$\varepsilon_i^{rot} = \frac{j^2}{I}. \quad (2.91)$$

In the quantum mechanical formulation that quantized the angular momentum j in units of $\frac{h}{2\pi}$ [2], the rotational kinetic energy levels of the rigid rotor are given by

$$\varepsilon_j^{rot} = \frac{j(j+1)h^2}{8\pi^2 I} \quad (2.92)$$

where j is the quantum number $j = 0, 1, 2, \dots$. Each energy level has a degeneracy of $2j + 1$ [7], so that the molecular partition function becomes

$$q^{rot} = \sum_{j=0}^{\infty} (2j+1) e^{-\frac{j(j+1)h^2}{8\pi^2 I k_B T}} \quad (2.93)$$

By defining a characteristic rotational temperature Θ^{rot} as abbreviation for

$$\Theta^{rot} = \frac{h^2}{8\pi^2 I k_B}, \quad (2.94)$$

the rotation partition function is

$$q^{rot} = \sum_{j=0}^{\infty} (2j+1) e^{-\frac{j(j+1)\Theta^{rot}}{T}}. \quad (2.95)$$

At the high temperature limit with $T \gg \Theta^{rot}$, Θ^{rot}/T becomes very small, so that the rotational energy levels are close together, and the sum can be approximated by an integral

$$q^{rot} = \int_0^{\infty} (2j+1) e^{-\frac{j(j+1)\Theta^{rot}}{T}} dJ \quad (2.96)$$

that gives

$$q^{rot} = \frac{T}{\Theta^{rot}} = \frac{8\pi^2 I k_B T}{h^2}. \quad (2.97)$$

which represents the classical limit of q^{rot} for fully excited rotation [4]. For diatomic molecules of pure compounds, i.e. symmetric molecules such as O_2 , N_2 etc., the rotation around 360° only gives distinguishable states for rotations up to 180° . Thus, a symmetry number σ is introduced that gives the number of undistinguishable states for a rotation around 360° [10]

$$q^{rot} = \frac{T}{\Theta^{rot} \sigma}. \quad (2.98)$$

with $\sigma = 2$ for symmetric diatomic molecules. At temperatures below the characteristic temperature for rotation, i.e. $\Theta^{rot} > 0.7 T$ [7], the rotational partition function can be directly determined from the summation in Eq. 2.95, considering $j = 0, 1, 2, 3$. For intermediate temperatures, approximations for the partition function of the rigid rotor are required, as discussed in the textbook by McQuarrie [7]. However, characteristic temperatures Θ^{rot} are generally quite low, as exemplary shown for some selected molecules in Table 2.2. Therefore, the rotational motion can be regarded as fully excited at ordinary temperatures.

For polyatomic molecules with three relevant moments of inertia I_{ii} with $i = x, y, z$, three characteristic rotational temperatures can be defined by [10]

$$\Theta_i^{rot} = \frac{h^2}{8\pi^2 k_B I_{ii}}. \quad (2.99)$$

Thus, the total rotational partition function becomes [10]

$$q^{rot} = \frac{1}{\sigma} \sqrt{\frac{\pi T^3}{\Theta_x^{rot} \cdot \Theta_y^{rot} \cdot \Theta_z^{rot}}}. \quad (2.100)$$

2.3.3 Partition Function of Vibrational Motion

In the classical approach, the partition function of vibrational motions is derived from the uncoupled contributions of its different vibrational degrees of freedom within the molecules, i.e. the vibrational normal modes. Assuming that the vibrational motion along a bond within a molecule is harmonic, the energy states of this (one-dimensional) harmonic oscillator i are

$$\varepsilon_{i,n}^{vib} = h\nu_i \left(n + \frac{1}{2} \right), \quad n = 0, 1, 2, \dots \quad (2.101)$$

where ν_i is the frequency of the vibration that depends on the force constant k_r of the bond. When m_1 and m_2 are the masses of the bonded atoms, a reduced mass can be defined [2]

$$m^* = \frac{m_1 \cdot m_2}{m_1 + m_2} \quad (2.102)$$

and the frequency of harmonic vibration is given by

$$\nu_i = \frac{1}{2\pi} \sqrt{\frac{k_{r,i}}{m^*}}. \quad (2.103)$$

It should be mentioned that the approximation of an harmonic vibration is only valid for low frequencies ν , i.e. moderate temperatures. For increasing ν , the potential energy curve becomes more anharmonic [2] and is better described by the Morse potential [5] (see Chap. 6). Introducing a characteristic temperature of vibration [10]

$$\Theta_i^{vib} = \frac{h\nu_i}{k_B}, \quad (2.104)$$

the partition function for this vibrational mode can be expressed as

$$q_i^{vib} = \sum_{n=0}^{\infty} e^{-\left(\frac{\Theta_i^{vib}(n+1/2)}{T}\right)} = e^{-\frac{\Theta_i^{vib}}{2T}} \sum_{n=0}^{\infty} e^{-\frac{n\Theta_i^{vib}}{T}}. \quad (2.105)$$

Therein the factor before the sum represents the ground state energy [2] that depends on the chosen ground state along the potential energy well. The sum can be evaluated

Table 2.2 Characteristic temperatures of rotation and vibration for some selected molecules with data from [7–9]. For polyatomic molecules, the range of characteristic temperatures for the different modes is provided

Molecule	$\Theta^{rot} (K)$	$\Theta^{vib} (K)$
H_2	85.2	6140
O_2	2.09	2260
N_2	2.88	3374
CO	2.77	3120
CO_2	0.561	954–3360
SO_2	0.495–2.92	750–1960
CH_4	7.54	1870–4320
H_2O	13.4–40.1	2290–5360

and gives

$$\sum_{n=0}^{\infty} e^{-nx} = \frac{1}{1 - e^{-x}}. \quad (2.106)$$

Thus, the vibrational partition function of an ideal harmonic oscillator becomes

$$q_i^{vib} = \frac{e^{-(\Theta_i^{vib}/2T)}}{1 - e^{-\Theta_i^{vib}/T}}. \quad (2.107)$$

The total vibrational partition function from the contributions of all vibrational normal modes is then

$$q^{vib} = \prod_i q_i^{vib}. \quad (2.108)$$

As exemplary shown for some molecules in Table 2.2, characteristic temperatures Θ^{vib} are in general very high, so that only the lowest vibrational energy level needs to be considered at ordinary temperatures [8].

2.3.4 Electronic and Nuclear Partition Function

Both the electronic and the nuclear partition function can be written as sum over the different electronic and nuclear energy levels ε_i [7]. When a specific energy level has a degeneracy of g_i (see Eq. 2.17), the partition function can be expressed as

$$q^{elec/nuc} = \sum_i g_i^{elec/nuc} e^{-\left(\frac{\varepsilon_i^{elec/nuc}}{k_B T}\right)}. \quad (2.109)$$

The first energy level is the ground state, i.e. $\varepsilon_1^{elec/nuc} = 0$.

In general the separations between electronic or nuclear energy levels are large compared to $k_B T$. Thus, for the electronic partition function, only the ground state and possibly the first excited state need to be considered at ordinary temperature. With $\Delta\varepsilon_{12}^{elec}$ being the energy difference between the ground state and the first excited state, the electronic partition function becomes [7]

$$q^{elec} = g_1^{elec} + g_2^{elec} e^{-\left(\frac{\Delta\varepsilon_{12}^{elec}}{k_B T}\right)}. \quad (2.110)$$

For the nuclear partition function no excited state needs to be included at terrestrial temperatures so that it is only given by the degeneracy of the ground state energy [7]

$$q^{nucl} = g_1^{nucl}. \quad (2.111)$$

2.4 Maxwell-Boltzmann Distribution of Velocities

The Maxwell-Boltzmann relation provides a probability distribution of the velocities of particles within a system as a function of the temperature. Equation (2.15) gives the probability that a particle has a specific energy ε_i . When the different energy states have degeneracies of g_j , the probability N_i/N of the energy state ε_i becomes

$$\frac{N_i}{N} = \frac{g_i e^{-\varepsilon_i/k_B T}}{\sum_j g_j e^{-\varepsilon_j/k_B T}}. \quad (2.112)$$

When the energy of a particle is its kinetic energy associated with the translational motion with the velocity v , ε_i is given by

$$\varepsilon_i = \frac{m}{2} v^2. \quad (2.113)$$

(see Sect. 2.3.1). Thus, the probability that any one particle has an energy between ε and $\varepsilon + d\varepsilon$ is

$$\frac{N(\varepsilon)}{N} = C g(\varepsilon) e^{-\varepsilon/k_B T} = C g(v) e^{-mv^2/2k_B T} = f(v) dv, \quad (2.114)$$

where $f(v)$ is the distribution function of the velocity v , and C is a proportionality factor.

For the velocity distribution, the translational motions in all three dimensions have to be taken into account with

$$v^2 = v_x^2 + v_y^2 + v_z^2. \quad (2.115)$$

Thus, all particles with the same velocity lie on the surface of a sphere with the radius v . Therefore, the number of particles having an energy between ε and $\varepsilon + d\varepsilon$ corresponds to the number of particles whose velocity vector ends in a spherical shell in velocity space with radius v and thickness dv [8]. With this, the degeneracy $g(v)$ is given by the volume of the spherical velocity shell

$$g(v) = 4\pi v^2 dv, \quad (2.116)$$

and the velocity distribution function then becomes

$$f(v) dv = 4\pi C v^2 e^{-mv^2/2k_B T} dv. \quad (2.117)$$

The proportionality factor C can be derived from the postulation that the integration of the velocity distribution function over all possible velocities has to yield $= 1$

$$\int_0^\infty f(v) dv = 4\pi C \int_0^\infty v^2 e^{-mv^2/2k_B T} dv = 1 \quad \rightarrow \quad C = \left(\sqrt{\frac{m}{2\pi k_B T}} \right)^3. \quad (2.118)$$

This finally gives the Maxwell-Boltzmann velocity distribution

$$f(v) dv = 4\pi \left(\sqrt{\frac{m}{2\pi k_B T}} \right)^3 v^2 e^{-mv^2/2k_B T} dv, \quad (2.119)$$

from which three characteristic velocities can be derived. The most probable velocity \hat{v} at a given temperature T results from the maximum of the distribution function

$$\frac{df(v)}{dv} = 0 \quad \rightarrow \quad \hat{v} = \sqrt{\frac{2k_B T}{m}}. \quad (2.120)$$

The mean velocity $\langle v \rangle$ is given by the integral over all possible velocities, weighted by the probability distribution $f(v)$

$$\langle v \rangle = \int_0^\infty v f(v) dv = \sqrt{\frac{8k_B T}{m\pi}}. \quad (2.121)$$

In the same way, the root mean square velocity $\langle v^2 \rangle$ can be determined

$$\langle v^2 \rangle = \int_0^\infty v^2 f(v) dv = \frac{3k_B T}{m}, \quad (2.122)$$

which relates the kinetic energy of a system to the temperature T . For a system of N particles, the total kinetic energy is

$$E_{kin} = \left\langle \sum^N \frac{m}{2} v^2 \right\rangle = N \frac{m}{2} \langle v^2 \rangle = \frac{3}{2} N k_B T. \quad (2.123)$$

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