Chapter 8
Statistical Thermodynamics

Abstract Using the concept of statistics and probability, statistical thermodynamics relates the state variables of macroscopic systems to the properties of its microscopic constituents. The state variables can be attributed to one single quantity: the partition function of the system.

The selection of problems in this chapter focuses primarily on the basic principles of probability calculus, as it is the prerequisite for a deeper understanding of statistical thermodynamics. The correct treatment of factorials (see Sect. A.3.9 in the appendix) is a frequently occurring technical issue that is addressed, for example, in Problem 8.3. Using the probability calculus, we see how the Boltzmann distribution can be motivated and how the phenomenon of diffusion can be understood. A second focus is on problems dealing with concrete cases of partition functions and their relation to thermodynamic quantities such as entropy or molar heat capacities.

8.1 Basic Concepts

In the following, it is assumed that the reader is familiar with basic stochastic calculus. Moreover, statistical thermodynamics makes use of the correct description of atoms and molecules within quantum mechanics (see Chap. 9).

8.1.1 Statistical Interpretation of Entropy

The statistical interpretation of entropy introduced by L. Boltzmann follows the notion that a system composed of many particles can take a very large number of states characterized by the individual positions and velocities and all other kinds of degrees of freedom of the molecular entities. These states of the system are called **microstates**. However, the system can in practice only be characterized by its total energy E or other macroscopic state variables. These constitute the spectrum of possible **macrostates**. For example, there is generally a large number of different microstates leading to the same total energy. If under certain conditions these microstates occur with equal probability, it is obvious that the macrostate comprising the highest number of different microstates is most likely to occur in

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reality, which means that the dynamics of the system have a tendency to reach this state. Such considerations led to the statistical definition of **entropy** S

$$S = k_B \ln W \tag{8.1}$$

where

$$W = \frac{N!}{\prod_i N_i!} \tag{8.2}$$

called **statistical weight** is the number of ways in which a macrostate can be realized, N is the number of particles, and N_i is the number of particles in the ith range of possible position and momentum.

8.1.2 Boltzmann Distribution

Consider a system of fixed composition at a fixed temperature T. A certain state i of the system has the energy ϵ_i. The probability of the state i is:

$$p_i = \frac{\mathrm{e}^{-\beta\epsilon_i}}{Q}; \qquad \beta = \frac{1}{k_B T} \tag{8.3}$$

with the partition function

$$Q = \sum_i \mathrm{e}^{-\beta\epsilon_i}; \qquad \beta = \frac{1}{k_B T}. \tag{8.4}$$

The goal is to determine macroscopic state variables such as internal energy U, the heat capacity C_V, or its entropy S from the system partition function Q.

8.1.3 Canonical Ensemble

For the statistical treatment of the system the **ensemble** concept is key, which was introduced by J.W. Gibbs. An ensemble is a collection of $\mathcal{N}$ identical copies of the system. The ensemble concept allows the treatment of systems comprising only a few molecules, or in an extreme case, only one single molecule. Moreover, by

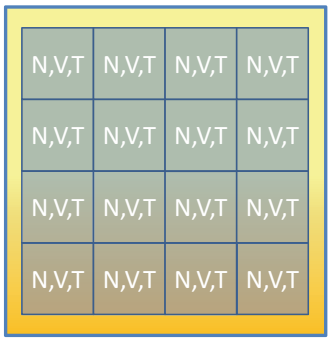

Fig. 8.1 Illustration of a canonical ensemble of $\mathcal{N} = 16$ copies of a system at a constant N, T, V. The walls of the systems are rigid and diathermic

choosing a large number $\mathcal{N}$ of copies, the application of Stirling's approximation to handle factorials is justified. If temperature T, volume V, and particle number N are constant in each of these copies, then the ensemble is called a **canonical ensemble**, and the partition function is called **canonical partition function**. Such a canonical ensemble is illustrated in Fig. 8.1 for small $\mathcal{N}$. The diathermic walls in the ensemble guarantee constant temperature in all copies of the system, but the energy fluctuates around the most probable energy value. At very large $\mathcal{N}$ the probability distribution has a very sharp peak. If q is the partition function of one copy of the system, then the partition function Q is obtained as a product over all $\mathcal{N}$ copies. Depending on whether or not these copies are distinguishable, the partition function is

$$Q = q^{\mathcal{N}} \qquad \text{distinguishable} \tag{8.5}$$

$$Q = \frac{1}{\mathcal{N}!} q^{\mathcal{N}} \qquad \text{indistinguishable} \tag{8.6}$$

The classification into distinguishable and indistinguishable units is frequently based on quantum mechanics in which the indistinguishability of identical particles is established. It has been pointed out, however, that in his early analysis of the Gibbs paradox, Gibbs argued on the basis of *operational distinguishability* on purely classical grounds [1]. It can be shown that the internal energy of the system, expressed using the canonical partition function, is

$$U = -\left(\frac{\partial \ln Q}{\partial \beta}\right)_{T,V} = k_B T^2 \left(\frac{\partial \ln Q}{\partial T}\right)_{T,V}; \qquad \beta = \frac{1}{k_B T}. \tag{8.7}$$

The entropy is

$$S = \left(\frac{d}{dT} \left(k_B T \ln Q \right) \right)_{V,T} \tag{8.8}$$

8.2 Molecular Degrees of Freedom and Partition Functions

Using the ensemble concept, the system partition function Q can be written as a product of molecular partition functions q (cf. Eqs. (8.5) and (8.6)). Using quantum mechanics, the molecular partition function can be separated into a product of partition functions associated with the various degrees of freedom, translation, rotation, vibrations, and electronic excitation[1]:

$$q_{\text{molecule}} = q_{\text{trans.}} q_{\text{rot.}} q_{\text{vib.}} q_{\text{el.}} \tag{8.9}$$

This assumes that the energy levels of the molecule can be written as the sum

$$E_{\text{molecule}} = E_{\text{trans.}} + E_{\text{rot.}} + E_{\text{vib.}} + E_{\text{el.}}. \tag{8.10}$$

For the calculation of the partition function associated with a special degree of freedom, the possibility of a g_i-fold **degeneracy** of an energy level ϵ_i has to be taken into account:

$$q = \sum_i g_i \, \mathrm{e}^{-\beta \epsilon_i}; \qquad \beta = \frac{1}{k_B T} \tag{8.11}$$

The quantum mechanical result for the translational part of the partition function obtained from the particle in a box model is, as textbooks show,

$$q_{\text{trans.}} = \frac{V}{\Lambda^3} = \frac{(2\pi m k_B T)^{\frac{3}{2}}}{h^3} V \tag{8.12}$$

[1] Strictly speaking, rotational and vibrational degrees of freedom are coupled in a molecule. In many cases, however, the treatment of a molecule as a rigid rotator with entirely harmonic vibrational modes is a useful approximation. It allows a separation of rotation and vibrational degrees of freedom.

where h is the Planck constant (see Sect. A.1), Λ is a *thermal wavelength*, and V is the system volume.

The rotational partition function of a heteronuclear diatomic is

$$q_{\text{rot}} = \sum_J (2J+1)\, \mathrm{e}^{-\beta hcBJ(J+1)}; \qquad \beta = \frac{1}{k_B T} \tag{8.13}$$

where J is the rotational quantum number and B is the rotational constant (see Sect. 10.1.2). Based on the harmonic oscillator model (see Sect. 10.1.3), the vibrational partition function of the diatomic takes a compact form:

$$q_{\text{vib.}} = \frac{\mathrm{e}^{-\beta \frac{h\nu}{2}}}{1 - \mathrm{e}^{-\beta h\nu}} \tag{8.14}$$

Here, ν is the vibrational frequency of the stretch vibration. In the case of polyatomic molecules, or in all cases beyond the harmonic oscillator model, the expressions are more complicated. Moreover, in symmetric molecules like H_2 or CO_2, nuclear spin statistics must also be considered when the molecular partition function is determined.

8.3 Problems

A further problem related to statistical thermodynamics is Problem 9.1 at page 221.

Problem 8.1 (Conformational Entropy and Protein Structure) Myoglobin (see Fig. 8.2) is a protein structure made of 150 amino acids. Assume that each of these subunits can take six different orientations, which in principle leads to a huge number of different conformer structures. Can you calculate this number? However, within the cellular environment, the protein has a well-defined structure. Assume that the latter is characterized by only one single conformation. Use Boltzmann's statistical definition of entropy (Eq. (8.1)) to calculate the protein's conformational entropy.

Solution 8.1 This problem is a simple application of Boltzmann's entropy formula. However, it illustrates the astonishing aspects of life on the molecular scale, and shows us an extreme example of thermodynamic stability. Myoglobin (Fig. 8.2) has a very complex structure and thus a huge number of internal degrees of freedom. In the cellular environment, the covalent bonds of the molecule can be considered

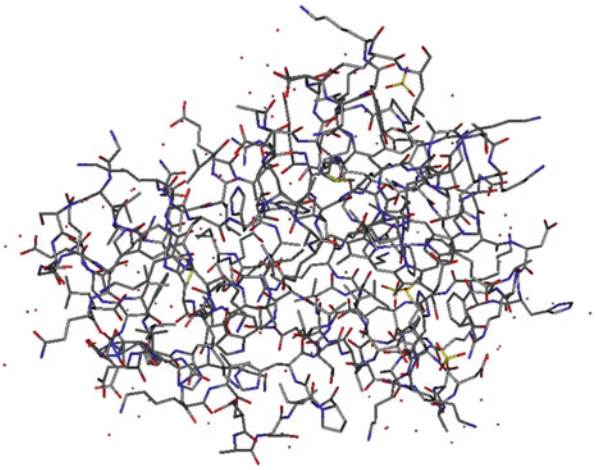

Fig. 8.2 Myoglobin protein structure

stable. If we leave the vibrational degrees of freedom aside, the conformations[2] of the molecule's substructure, the amino acids, are most important. For simplicity, we assume that each amino acid has six possible conformations. For two amino acids, there is a total of $6 \times 6 = 36$ different conformations; for 150 amino acids, we have

$$N = 6^{150} \tag{8.15}$$

different structures. A conventional pocket calculator cannot display this number in the usual way. What we can do is to rewrite this number as follows:

$$N = 6^{150} = 10^x \Leftrightarrow x = \frac{150 \ln 6}{\ln 10} = 116.7226878$$

Thus,

$$N = 10^{116.7226878} = 10^{116} 10^{0.7226878} = 5.280655064 \times 10^{116}. \tag{8.16}$$

An astonishing fact about the molecule is that under cellular conditions the molecule only occurs in a few well-defined conformational structures characterized by a few special sequences out of 6^{150}. For simplicity, we assume that there is only one such functional form of the molecule. If the molecule had to find this unique structure in a random-walk process where each conformational change takes only a few picoseconds, this process would take a very long time. In contrast, real folding times are less than 1 s [2]. This discrepancy is called *Levinthal paradox*.

[2]The switching of a molecule between different conformations has been treated in Problem 5.3.

Moreover, if the folding process were driven by the minimization of the Gibbs free energy $\Delta G = \Delta H - T\Delta S$ of the molecule, then this unique functional form would have to be characterized by a steep minimum in enthalpy that balances the large entropic contribution $-T\Delta S$ to ΔG, where ΔS is the conformational entropy. It is our task to calculate this entropy using Boltzmann's statistical approach to entropy. We assume two macrostates: (1) the functional state, which is realized by $W_1 = 1$ configuration of the molecule, and (2) the dysfunctional state, realized by all remaining $W_2 = N-1$ conformational sequences. As N is so large, we can safely assume $W_2 = N$. Thus,

$$\Delta S = S_{\text{functional}} - S_{\text{disfunctional}} = N_A k_B \ln W_1 - N_A k_B \ln W_2 \tag{8.17}$$

Using $N_A k_B = R = 8.3145\,\text{J}\,\text{K}^{-1}\,\text{mol}^{-1}$ and $\ln W_1 = \ln 1 = 0$, we obtain

$$\Delta S = -2235\,\text{J}\,\text{K}^{-1}\,\text{mol}^{-1}.$$

To compensate for this decrease in entropy during the folding process, therefore, the room temperature enthalpy change must be at least below $\Delta H = 298K \times \Delta S = -666\,\text{kJ}\,\text{mol}^{-1}$.

Problem 8.2 (Mixing of Gases) Consider the arrangement of two compartments I and II with the same volume V, as shown in Fig. 8.3. Initially, the compartments are separated by a baffle and contain an equal number of particles of two different species, which may be treated as a perfect gas. If the baffle is removed the gas particles may change the compartment. Assume $N = 4$ particles of each species, as shown in the figure.

a. Calculate the probability that all particles of whatever species are located in compartment I.
b. What is the probability of finding all particles of species B (dark balls) in compartment I, and all particles of the other species G (white balls) in compartment II?
c. Draw a probability distribution of finding n particles of species B ($n = 0, \ldots, 4$) in compartment I. Draw a probability distribution of finding n particles of whatever species ($n = 0, \ldots, 2N$) in compartment A.

Solution 8.2 This exercise gives a rather elementary demonstration of the mixing of gases and how it is related to the basic principles of probability.[3] The initially separated gases in the two compartments I and II comprise only four particles. This enables us to write down all possibilities regarding how the particles can be

[3] We have dealt with a thermodynamical description of gas mixing in Chap. 3, Problem 3.7.

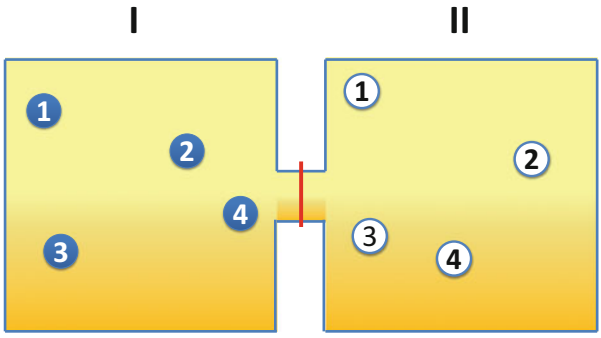

Fig. 8.3 Two compartments filled with different gases, separated by a baffle

distributed in the compartments after the baffle is removed. In our solution, we use the following notation to indicate a special configuration of particles: we use the number 1 to indicate when a particle is found in compartment I, and the number 0 if it is in compartment II. The initial configuration as shown in Fig. 8.3 is:

$$1111, 0000$$

i.e., the first four numbers indicate the positions of the species B (the dark balls) with label 1, 2, 3, and 4. The next four numbers give the positions of the particles 1, 2, 3, and 4 of species G (white balls).

In **subproblem (a)**, we give the probability that all particles, no matter whether they belong to species G or species B, are found in compartment I. This is the configuration:

$$1111, 1111.$$

In a perfect gas, the particles do not interact; thus, their movements are independent, and the probability of finding one special particle, say B1 (dark ball with label 1), is $p = \frac{1}{2}$. Either it is found in compartment I, or, with the same probability $\frac{1}{2}$, it is found in compartment II. As the particles move independently, the presence of particles in the compartment does not influence the probability of finding the other particles in the compartment. All particles have the same probability $\frac{1}{2}$, and the joint probability for this configuration is thus:

$$p(1111, 1111) = \left(\frac{1}{2}\right)^{2N} = \left(\frac{1}{2}\right)^{8} = 3.9 \times 10^{-3}. \tag{8.18}$$

The probability is small, but not too small. Statistically, 1 in 256 measurements would yield this configuration. However, if the total number of particles were increased to $2N = 100$, the probability of finding all the particles in compartment

I would be within the range 10^{-30}. For realistic particle numbers $N \approx 10^{23}$, the probability of this event is *de facto* zero.

In **subproblem (b)**, we give the probability of finding all particles of species B in compartment I and all particles of species G in compartment II. This event is in fact the initial configuration. It has the same probability as any of the possible $2^{2N} = 256$ configurations. The probability is, therefore:

$$p(1111, 0000) = \left(\frac{1}{2}\right)^8 = 3.9 \times 10^{-3}. \tag{8.19}$$

Thus, the event of a perfect separation of the gases is rare; when limited to realistic particle numbers, it is unimaginably small.

In **subproblem (c)**, we generate a probability distribution of finding n particles of species B in compartment 1, where n is 0, 1, 2, 3, or 4. These events represent in general several possible configurations. We can write them down explicitly:

$$\left.\begin{array}{l} 0000 \end{array}\right\} n = 0$$

$$\left.\begin{array}{l} 1000 \\ 0100 \\ 0010 \\ 0001 \end{array}\right\} n = 1$$

$$\left.\begin{array}{l} 1100 \\ 1010 \\ 1001 \\ 0110 \\ 0101 \\ 0011 \end{array}\right\} n = 2$$

$$\left.\begin{array}{l} 1110 \\ 1101 \\ 1011 \\ 0111 \end{array}\right\} n = 3$$

$$\left.\begin{array}{l} 1111 \end{array}\right\} n = 4$$

If we define the statistical weight as the number of configurations for an event, $W(n)$, then we have $W(0) = W(4) = 1$, $W(1) = W(3) = 4$, and $W(2) = 6$. Because all the $Z = 2^N = 2^4 = 16$ configurations are assumed to appear with the same probability, the joint probability for the event n particles in compartment I is

$$p(n) = \frac{W(n)}{Z}. \tag{8.20}$$

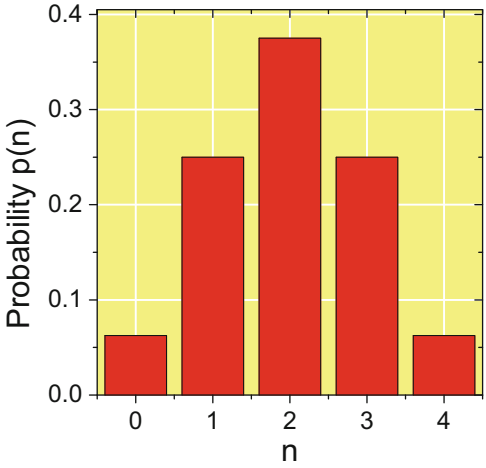

Fig. 8.4 Probability distribution for the event of finding n particles of species B in compartment I

The resulting probabilities are depicted in Fig. 8.4. Two particles of species B being found in compartment I is the most probable event, which shows that there is a tendency that half of the particles are found in compartment I, the other half in compartment II. In terms of thermodynamics, the gas undergoes a free expansion into the total accessible volume after the baffle is removed. Limited to realistically large particle numbers, the event $n = \frac{N}{2}$ is dominant. If we want to show this[4], we need an equation for the statistical weight $W(n)$ for arbitrary N. Our elementary analysis for $N = 4$ above shows that $W(n)$ is just the number of possible *permutations* of a sequence of numbers. In our case $W(n)$ is given by (see Eq. (8.2))

$$W(n) = \frac{N!}{n!\,(N-n)!}. \tag{8.21}$$

With this relation, it is straightforward to generate the second probability distribution of finding n particles of whatever species in compartment I. With the total number of $2N = 8$ particles, the probabilities are:

$$p(n) = \frac{(2N)!}{2^{2N} n!\,(2N-n)!} = \frac{8!}{2^8 n!\,(8-n)!} \tag{8.22}$$

The resulting distribution is shown in Fig. 8.5.

The distribution has a maximum, as expected, at $n = 4$. Note that in the limiting case of identical species B and G, nothing happens from the macroscopic point of view if the baffle is removed. This is the origin of the Gibbs paradox, which

[4]The dominant event $n = \frac{N}{2}$ would have the probability $p\left(\frac{N}{2}\right) = \frac{N!}{2^N \left(\frac{N}{2}\right)! \left(\frac{N}{2}\right)!}$. Consideration of $\ln p\left(\frac{N}{2}\right)$ and Stirling's formula Eq. (A.62) yields $\ln p\left(\frac{N}{2}\right) = 0$ and thus $p\left(\frac{N}{2}\right) = 1$.

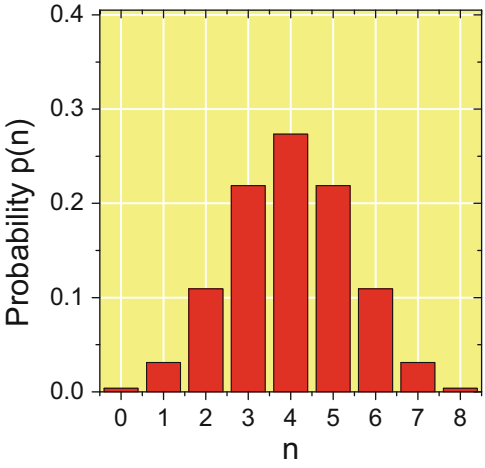

Fig. 8.5 Probability distribution for the event of finding n particles of whatever species in compartment I

deals with the entropy of mixing of identical species. Straightforward application of Eq. (3.35) would yield a positive entropy of mixing, even in the case of identical species, although no macroscopic change of state occurs. Based on our simple model of gas mixing we cannot analyze this in more detail; in particular, the calculation of entropy changes of the gases must be based on Eq. (8.8). In summary, we have seen in a very simplified case how statistics governs the distribution of independently moving gas particles.

Problem 8.3 (A Simple Model of Diffusion) Being initially located at $x = 0$, a molecule takes discrete steps in one dimension with a step length a. With the same probability, it takes a step to the right (R) or to the left (L). For example, a possible hopping sequence with eight steps is LRRLLLRL, leaving the molecule at the position $x = -2a$.

a. Show that probability of finding the molecule after N steps at position m is

$$P_N(m) = \left(\frac{1}{2}\right)^N \frac{N!}{\left(\frac{N+m}{2}\right)!\,\left(\frac{N-m}{2}\right)!} \tag{8.23}$$

b. Plot $P_N(m)$ for $N = 4, 5, 8$.

c. Show that for large N the probability of finding the molecule at position m is

$$P_N(m) = \frac{2}{\sqrt{2\pi N}} \exp\left(-\frac{m^2}{2N}\right) \tag{8.24}$$

(continued)

Problem 8.3 (continued)
and give an interpretation of this result. *Hint*: Use Stirling's approximation $\ln n! = \left(n + \frac{1}{2}\right) \ln n - n + \ln \sqrt{2\pi}$ (see Eq. (A.63)) and the Taylor expansion Eq. (A.56).

Solution 8.3 In this problem, we apply the principles of probability and statistics to a simple model of molecular diffusion processes in one dimension. **Diffusion** is a prime example of an irreversible process. How does irreversibility occur in a process that is a sequence of individual reversible steps? In **subproblem (a)**, we work out the expression for the probability that a molecule is found at a certain position m after N steps on a discrete lattice in one dimension. The situation is illustrated in Fig. 8.6 for the special path sequence given in the problem formulation, LRRLLLRL. As every step to the right or to the left occurs with the same probability, $\frac{1}{2}$, the joint probability for this special 8-step sequence is $\left(\frac{1}{2}\right)^8$. For a special N-step sequence, the joint probability is $\left(\frac{1}{2}\right)^N$. This special sequence puts the molecule in its final position at $x = -2a$. However, this is not the only sequence that produces this result. For example, the sequence RLRLLLRL would also put the molecule in this final position. Clearly, the total number of steps to the right (R) and steps to the left (L) is decisive with regard to the final position. If there are n steps to the right, then we have $N - n$ moves to the left. Among the 2^N different sequences with N steps, there are

$$Z_N(n) = \frac{N!}{n!\,(N-n)!} \tag{8.25}$$

sequences with n steps to the right. We have to add up the probabilities of each sequence among this subset and obtain the probability that the molecules move n steps to the right:

$$P_N(n) = \sum_i^{Z_N(n)} \left(\frac{1}{2}\right)^N = \left(\frac{1}{2}\right)^N \frac{N!}{n!\,(N-n)!} \tag{8.26}$$

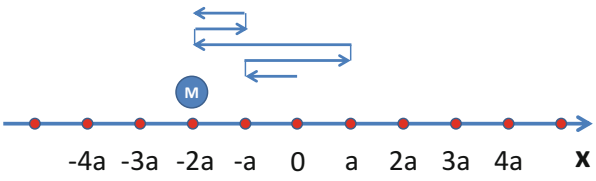

Fig. 8.6 Discrete movement of a molecule "M" in one dimension. After an eight-step hopping sequence, LRRLLLRL, the molecule is situated at $x = -2a$ with a being the step length

In the next step, we have to analyze at which position the molecule is placed after a N-step sequence with n steps to the right and $N - n$ steps to the left. Each step to the right increases the position index m by one, while m is reduced by one in a step to the left. As a consequence, after N steps, the position index is

$$m = (n - (N - n)) = 2n - N. \tag{8.27}$$

Hence, the number of steps to the right leading to the special position index m is:

$$n = \frac{N + m}{2}. \tag{8.28}$$

If we insert this result into Eq. (8.26) we obtain:

$$P_N(m) = \left(\frac{1}{2}\right)^N \frac{N!}{(\frac{N+m}{2})!\,(N - \frac{N+m}{2})!} = \left(\frac{1}{2}\right)^N \frac{N!}{(\frac{N+m}{2})!\,(\frac{N-m}{2})!} \tag{8.29}$$

which is simply the expression Eq. (8.23). It is worth inspecting Eq. (8.27) again: if we have an even total number of steps ($N = 2K$, $K = 0, 1, 2, \ldots$), then $m = 2n - 2K = 2(n - K)$ will also be even. Therefore, an even total number of steps places the molecule at an even position, $m = 0, \pm 2, \pm 4, \ldots$. Conversely, if the total number of steps is odd, then m will also be odd and the molecule reaches $m = \pm 1, \pm 3, \ldots$. This notion is important for the correct interpretation of the results in subproblem (c), but also for the plotting of the probabilities in **subproblem (b)** for $N = 4, 5, 8$. For $N = 4$, the possible end points are $m = \pm 2, \pm 4$. Evaluation of the associated probabilities using Eq. (8.23) yields:

$$P_4(\pm 2) = \left(\frac{1}{2}\right)^4 \frac{4!}{3!\,1!} = 0.25 \qquad P_4(\pm 4) = \left(\frac{1}{2}\right)^4 \frac{4!}{4!\,0!} = 0.0625$$

Moreover, we have:

$$P_4(\pm 0) = \left(\frac{1}{2}\right)^4 \frac{4!}{2!\,2!} = 0.375$$

We can check if P_4 is normalized by adding all probabilities and obtain:

$$\sum_m P_4(m) = 0.0625 + 0.25 + 0.375 + 0.25 + 0.0625 = 1$$

As expected, this discrete probability distribution is normalized. In the same way, we can calculate the possible values for the requested distributions P_5 and P_8. The results are illustrated in Fig. 8.7. Inspection of the plots reveals that the probability of finding the molecule in the center (low values of m) is highest, whereas high absolute values of m have decreasing probability. Moreover, the bell-shaped profile of the

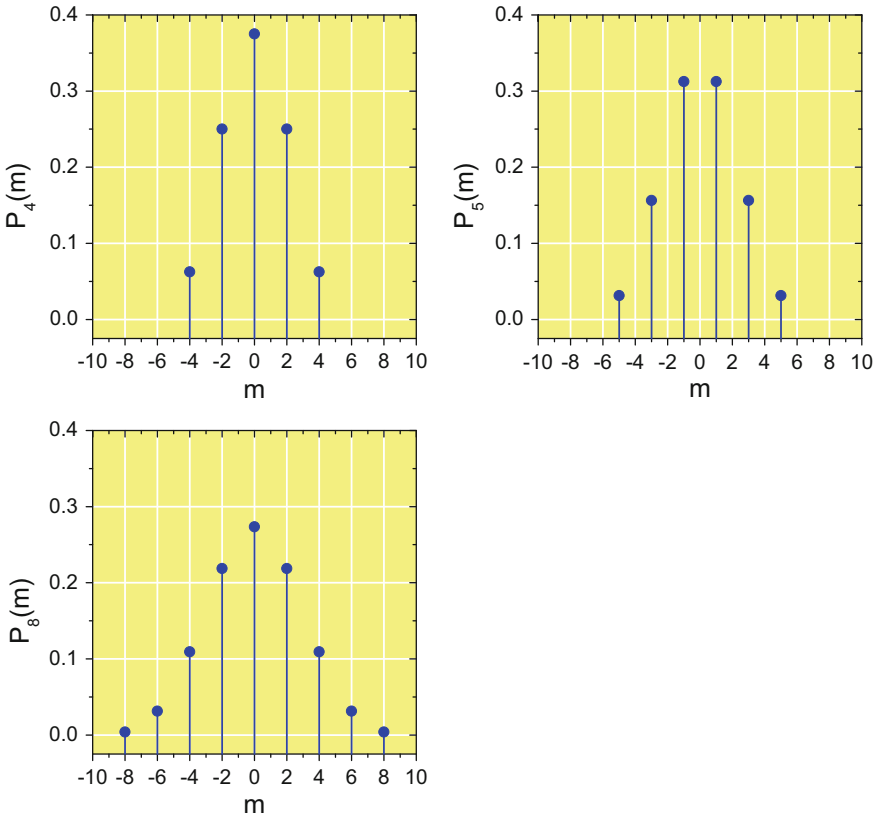

Fig. 8.7 Probability distributions $P_N(m)$ for $N = 4, 5, 8$

distribution is especially apparent in the case of P_8. This suggests that for a large total number of steps, the distribution could take the Gaussian shape of a normal distribution as illustrated in the appendix in Fig. A.2. This limiting case is examined in **subproblem (c)**. We prove that Eq. (8.23) is identical to Eq. (8.24) when limited to high N. This task is instructive because we learn how to cope with factorials using *Stirling's approximation*. This sort of calculus is typical for problems occurring in statistical thermodynamics. For large N, the factorial $N!$ is[5]

$$N! \approx \left(\frac{N}{e}\right)^N \sqrt{2\pi N} \tag{8.30}$$

and thus

[5]Note that in some textbooks you might find a less precise version of Stirling's formula: $\ln N! \approx N \ln N - N$ which, in the present problem would not yield the correct prefactor containing $\sqrt{2\pi N}$.

$$\ln N! \approx \left(N + \frac{1}{2}\right) \ln N - N + \frac{1}{2} \ln \sqrt{2\pi} \tag{8.31}$$

Using Eq. (8.31) and the rules for logarithms in the appendix (Sect. A.3.3), we write

$$\begin{aligned}
\ln P_N(m) &= N \ln \frac{1}{2} + \ln N! - \ln \left(\frac{N+m}{2}\right)! - \ln \left(\frac{N-m}{2}\right)! \\
&= N \ln \frac{1}{2} + \left(N + \frac{1}{2}\right) \ln N \; -N \; + \ln \sqrt{2\pi} \\
&\quad - \left(\frac{N+m}{2} + \frac{1}{2}\right) \ln \frac{N+m}{2} \; + \frac{N+m}{2} \; - \ln \sqrt{2\pi} \\
&\quad - \left(\frac{N-m}{2} + \frac{1}{2}\right) \ln \frac{N-m}{2} \; + \frac{N-m}{2} \; - \ln \sqrt{2\pi}
\end{aligned}$$

The three highlighted terms cancel each other out. Further evaluation yields:

$$\begin{aligned}
\ln P_N(m) &= N \ln \frac{1}{2} + \left(N + \frac{1}{2}\right) \ln N - \ln \sqrt{2\pi} \\
&\quad - \left(\frac{N+m+1}{2}\right) \left[\ln(N+m) + \ln \frac{1}{2}\right] \\
&\quad - \left(\frac{N-m+1}{2}\right) \left[\ln(N-m) + \ln \frac{1}{2}\right] \\
&= \; N \ln \tfrac{1}{2} \; + \left(N + \frac{1}{2}\right) \ln N - \ln \sqrt{2\pi} \\
&\quad \; -\tfrac{N}{2} \ln \tfrac{1}{2} \; -\tfrac{m}{2} \ln \tfrac{1}{2} - \frac{1}{2} \ln \frac{1}{2} \; -\tfrac{N}{2} \ln \tfrac{1}{2} \; +\tfrac{m}{2} \ln \tfrac{1}{2} - \frac{1}{2} \ln \frac{1}{2} \\
&\quad - \left(\frac{N+m+1}{2}\right) \ln N \left(1 + \frac{m}{N}\right) - \left(\frac{N-m+1}{2}\right) \ln N \left(1 - \frac{m}{N}\right)
\end{aligned}$$

Again, the highlighted terms cancel each other out.

$$\begin{aligned}
\ln P_N(m) &= \left(N + \frac{1}{2}\right) \ln N - \ln \sqrt{2\pi} - \ln \frac{1}{2} \\
&\quad - \left(\frac{N+m+1}{2}\right) \ln N - \left(\frac{N-m+1}{2}\right) \ln N \\
&\quad - \left(\frac{N+m+1}{2}\right) \ln \left(1 + \frac{m}{N}\right) - \left(\frac{N-m+1}{2}\right) \ln \left(1 - \frac{m}{N}\right)
\end{aligned}$$

$$
\begin{aligned}
&= N\ln N + \frac{1}{2}\ln N - \ln\sqrt{2\pi} - \ln\frac{1}{2} \\
&\quad -\tfrac{N}{2}\ln N \; -\tfrac{m}{2}\ln N - \frac{1}{2}\ln N \; -\tfrac{N}{2}\ln N \; +\tfrac{m}{2}\ln N - \frac{1}{2}\ln N \\
&\quad - \left(\frac{N+m+1}{2}\right)\ln\left(1+\frac{m}{N}\right) - \left(\frac{N-m+1}{2}\right)\ln\left(1-\frac{m}{N}\right)
\end{aligned}
$$

Highlighted terms cancel each other out. Further simplification using the rules for logarithms is not possible. However, the terms $\ln\left(1 \pm \frac{m}{N}\right)$ can be expanded in a power series according to Eq. (A.56) in the appendix:

$$
\ln\left(1 \pm \frac{m}{N}\right) = \pm\frac{m}{N} - \frac{m^2}{2N^2} + \cdots \tag{8.32}
$$

For large N, the power series can be truncated. However, at this point it is important to collect *all* terms up to the second order. If we were to truncate the expansion after the first term, then we would lose some quadratic terms in m. Therefore, we insert the expansion truncated after the second term and obtain:

$$
\begin{aligned}
\ln P_N(m) &= -\frac{1}{2}\ln N - \ln\sqrt{2\pi} - \ln\frac{1}{2} \\
&\quad - \left(\frac{N+m+1}{2}\right)\left(\frac{m}{N} - \frac{m^2}{2N^2}\right) - \left(\frac{N-m+1}{2}\right)\left(-\frac{m}{N} - \frac{m^2}{2N^2}\right) \\
&= -\frac{1}{2}\ln N - \ln\sqrt{2\pi} - \ln\frac{1}{2} \\
&\quad - \frac{N}{2}\frac{m}{N} - \frac{m^2}{2N} - \frac{m}{2N} + \frac{m^2}{4N} + \frac{m^3}{4N^2} + \frac{m^2}{4N^2} \\
&\quad + \frac{N}{2}\frac{m}{N} - \frac{m^2}{2N} + \frac{m}{2N} + \frac{m^2}{4N} - \frac{m^3}{4N^2} + \frac{m^2}{4N^2} \\
&= -\frac{1}{2}\ln N - \ln\sqrt{2\pi} - \ln\frac{1}{2} - \frac{m^2}{2N} + \frac{m^2}{2N^2}
\end{aligned}
$$

For large N, the last term becomes small and can be ignored. Rearranging then yields

$$
\ln\left(P_N(m)\sqrt{2\pi N}\frac{1}{2}\right) = -\frac{m^2}{2N} \tag{8.33}
$$

and thus

$$P_N(m) = \frac{2}{\sqrt{2\pi N}} \exp\left(-\frac{m^2}{2N}\right) \tag{8.34}$$

which is simply the expression that was to be proven.

This distribution function has a Gaussian shape, suggesting a normal distribution function[6] for the probability density $W(x)$ limited to large N and small a. With this limitation, the discrete lattice of locations $x = ma$ becomes continuous. Moreover, we can associate the total step number with time if we let $t = N\tau$, where τ is the hopping time of the molecule. The hopping interval is $\Delta x = 2a$, as discussed above in subproblem (a) (see also Fig. 8.7). Now, as $W(x, t)\, dx$ is the probability of finding the molecule between x and $x + dx$ at time t,

$$W(x,t) = \frac{P_N(m)}{2a} = \frac{1}{\sqrt{2\pi N a^2}} \exp\left(-\frac{m^2}{2N}\right) = \frac{1}{\sqrt{2\pi a^2 \frac{t}{\tau}}} \exp\left(-\frac{x^2}{2a^2 \frac{t}{\tau}}\right) \tag{8.35}$$

which is in fact a normal distribution. Note that the continuum limit requires that $a \to 0$ and $\tau \to 0$ in a way that $\frac{a^2}{\tau}$ is constant. Then, the variance of the distribution function,

$$\sigma^2 = \frac{a^2 t}{\tau}, \tag{8.36}$$

increases with time, consistent with an irreversible *diffusion process* of the molecule. It is common to introduce the *diffusion constant* D:

$$\sigma^2 = 2Dt. \tag{8.37}$$

Hence the probability density function takes the form:

$$W(x,t) = \frac{1}{\sqrt{4\pi Dt}} \exp\left(-\frac{x^2}{4Dt}\right) \tag{8.38}$$

This probability density function is a solution of Fick's second law:

$$\frac{\partial\, W(x,t)}{\partial t} = D \frac{\partial^2\, W(x,t)}{\partial x^2} \tag{8.39}$$

A generalization of the diffusion of the molecule in three dimensions is straightforward. The random walk approach to diffusion we have worked out in this problem

[6] See Eq. (A.64).

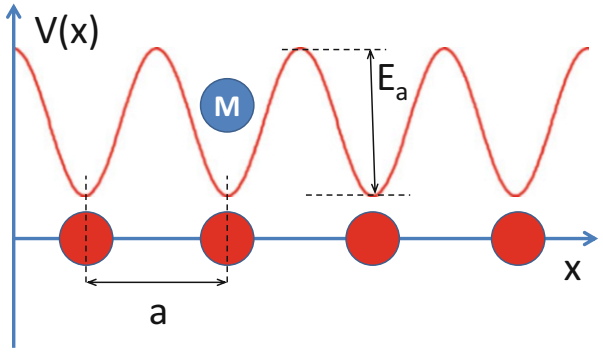

Fig. 8.8 Simplified one-dimensional model of a molecule M adsorbed on a surface. E_a is the activation energy for surface diffusion in the periodic potential $V(x)$, a the lattice parameter of the surface

is instructive in conjunction with the origin of irreversibility: even though each elementary step of the molecule is in principle a reversible operation, a sequence of such steps statistically introduces irreversibility.

Problem 8.4 (Surface Diffusion) *Hint: This problem presumes that you have dealt with Problem 8.3.*

At a temperature of 80 K, a molecule is adsorbed on a strictly periodic surface (see Fig. 8.8). The lattice constant of the surface is $a = 6 \times 10^{-10}$ m. The activation energy for surface diffusion is $E_a = 8.5\,\mathrm{kJ\,mol^{-1}}$, the attempt frequency (= frequency of frustrated lateral translations) is 1 THz.

a. Use Eqs. (8.35)–(8.37) and give an expression for the diffusion coefficient of the molecule as a function of temperature in one dimension.
b. Calculate the expectation values $\langle x \rangle$ and $\langle x^2 \rangle$ for the distance and the square of the distance of the molecule from its original adsorption site after 1 min.
c. What is the probability of finding the molecule after 60 s between $x = -\frac{a}{2}$ and $x = +\frac{a}{2}$, i.e., within the adsorption site from which the random walk starts?

Solution 8.4 Here, we deal with a concrete example of the random walk approach to diffusion on surfaces. On the atomic scale, single crystals have a periodic structure. At the interface, the periodicity is canceled in the dimension perpendicular to the surface, but the periodicity in the other two lateral dimensions is often maintained on mesoscopic length scales. This is demonstrated, for example, in atomic resolution scanning tunneling spectroscopy (STM) experiments, or, in the case of insulating materials, in scanning force microscopy (SFM) experiments.

Nowadays, these *surface science* techniques have reached a resolution that detects single molecules and maps their movements from scan to scan [3]. Molecules can be bound to a surface, either by *chemisorption* (covalent bonding, binding energies $>50\,\mathrm{kJ\,mol^{-1}}$), or by *physisorption* (weak van der Waals forces, binding energies $<50\,\mathrm{kJ\,mol^{-1}}$). Decisive for the molecule's mobility - quite often the prerequisite for surface chemical reactions to occur - is the depth of the lateral potential the molecule faces. For simplicity, we identify the well depth of the lateral potential with the activation energy for diffusion, $E_a = 8.5\,\mathrm{kJ\,mol^{-1}}$. Attempts of the molecule to move to a neighboring adsorption site are lateral frustrated translations with a restoring force that is mediated by the lateral potential. In our example, the frequency of this degree of freedom is $\nu_0 = 1\,\mathrm{THz}$.

In **subproblem (a)**, we derive an expression for the diffusion coefficient D introduced in the discussion of Problem 8.3(c). According to Eqs. (8.36) and (8.37), the diffusion constant is given by

$$D = \frac{a^2}{2\tau} \tag{8.40}$$

where τ is the time for one elementary step of the molecule. It is obvious that the hopping of the molecule from one site to the next site is itself a statistical process and τ has the nature of an average time that is influenced by temperature. If the number of hopping attempts is ν_0, this frequency has to be multiplied with a Boltzmann factor $\exp\left(-\frac{E_a}{RT}\right)$ to obtain the number of successful attempts:

$$\nu = \frac{1}{\tau} = \nu_0 \exp\left(-\frac{E_a}{RT}\right). \tag{8.41}$$

As a consequence, our expression for the diffusion constant as a function of temperature is:

$$D = \frac{a^2\nu_0}{2} \exp\left(-\frac{E_a}{RT}\right) \tag{8.42}$$

At a temperature of 80 K, we obtain

$$\begin{aligned} D &= \frac{\left(6.0 \times 10^{-10}\,\mathrm{m}\right)^2 \times 10^{12}\,\mathrm{s^{-1}}}{2} \times \exp\left(-\frac{8500\,\mathrm{J\,mol^{-1}}}{8.3145\,\mathrm{J\,K^{-1}\,mol^{-1}} \times 80\,\mathrm{K}}\right) \\ &= 5.08 \times 10^{-13}\,\mathrm{m^2\,s^{-1}}. \end{aligned}$$

In **subproblem (b)**, we answer how far the molecule will come statistically after a 1 min random walk, assuming the continuum approximation Eq. (8.35). It has been stressed in the solution of Problem 8.3 that the probability density distribution

$$W(x,t) = \frac{1}{\sqrt{4\pi Dt}} \exp\left(-\frac{x^2}{4Dt}\right) \tag{8.43}$$

is normalized, i.e.,

$$\int_{-\infty}^{+\infty} W(x,t)\,dx = 1. \tag{8.44}$$

The expectation value $\langle x\rangle$, also called the *first moment* of W is:

$$\langle x\rangle = \int_{-\infty}^{+\infty} x\,W(x,t)\,dx = 0. \tag{8.45}$$

This is because $W(x,t)$ is symmetrical with regard to the variable x: $W(x,t) = W(-x,t)$, while at the same time the integral $xW(x,t)$ is asymmetrical. Therefore, we must look at the *second moment* of the distribution, $\langle x^2\rangle$. As $W(x,t)$ is symmetrical:

$$\begin{aligned}
\langle x^2\rangle &= \int_{-\infty}^{+\infty} x^2 W(x,t)\,dx \\
&= 2\int_{0}^{+\infty} x^2 W(x,t)\,dx \\
&= 2\int_{0}^{+\infty} x^2 \frac{1}{\sqrt{4\pi Dt}} \exp\left(-\frac{x^2}{4Dt}\right) dx \\
&\overset{\text{Eq. (A.47)}}{=} \frac{2\sqrt{\pi}\,(4Dt)^{\frac{3}{2}}}{4\sqrt{4\pi Dt}} = 2Dt = 2\times 5.08\times 10^{-13}\,\mathrm{m^2\,s^{-1}}\times 60\,\mathrm{s} \\
&= 6.1\times 10^{-11}\,\mathrm{m^2}
\end{aligned}$$

Thus, $\langle x^2\rangle$ is the spatial variance σ^2 of $W(x,t)$ at time t (see Eq. (8.36)), and its standard deviation is $\sigma = \sqrt{\langle x^2\rangle} = 7.8\times 10^{-6}\,\mathrm{m}$. This corresponds to 13,000 unit cells. Hence, even at 80 K, the molecule is quite mobile on the surface. The corresponding profile of the probability of finding the molecule between location x and $x + dx$ after this time is illustrated in Fig. 8.9.

In **subproblem (c)**, we determine the probability of finding the molecule after 1 min at its original site, i.e., between $x = -\frac{a}{2}$ and $x = \frac{a}{2}$. Note that $x = 0$, the center of the distribution, has the highest probability density. The probability sought is a *cumulative* probability, similar to what we discussed in Problem 7.2 or in Problem 9.14c in connection with quantum mechanical probability. The cumulative probability is the definite integral:

$$\begin{aligned}
p(t) &= \int_{-\frac{a}{2}}^{+\frac{a}{2}} W(x,t)\,dx \\
&= \int_{-\frac{a}{2}}^{+\frac{a}{2}} \frac{1}{\sqrt{4\pi Dt}} \exp\left(-\frac{x^2}{4Dt}\right) dx
\end{aligned}$$

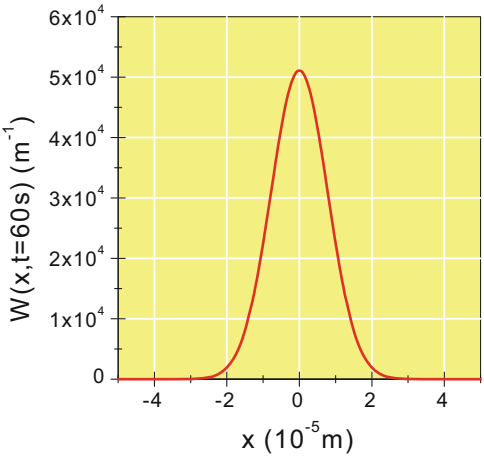

Fig. 8.9 Probability density function $W(x, t)$ of a molecule after a 60 s random walk

Again, we can use the fact that $W(x, t)$ is symmetrical with regard to x. Therefore,

$$p(t) = \frac{2}{\sqrt{4\pi Dt}} \int_0^{+\frac{a}{2}} \exp\left(-\frac{x^2}{4Dt}\right) dx$$

The substitution $u = \frac{x}{\sqrt{4Dt}}$ transforms[7] the integral into a form that can be related to the *error function* $\mathrm{erf}(u)$:

$$p(t) = \frac{2}{\sqrt{\pi}} \int_0^{+\frac{a}{2\sqrt{4Dt}}} \exp\left(-u^2\right) du \overset{\text{Eq. (A.50)}}{=} \mathrm{erf}\left(\frac{a}{4\sqrt{Dt}}\right) \tag{8.46}$$

The function $p(t)$ is shown in Fig. 8.10 for arbitrary time t between 0 and 60 s, calculated with the given value of $a = 6 \times 10^{-10}$ m and the diffusion constant obtained above: $D = 5.08 \times 10^{-13}\,\mathrm{m^2\,s^{-1}}$. As expected, $p(0)$ equals 1 and reaches within 1 s a value of 2×10^{-4}. After 60 s the probability is $p(60\,\mathrm{s}) = 3.1 \times 10^{-5}$. This means that statistically only 1 in 30,000 experiments would detect the molecule at its initial site.

Problem 8.5 (Derivation of Boltzman Distribution) Consider two identical systems A and B with diathermic walls in equilibrium at constant temperature (see Fig. 8.11). The probability of measuring the energy E_A in

(continued)

[7] The differential dx is thus $dx = \sqrt{4Dt}\,du$.

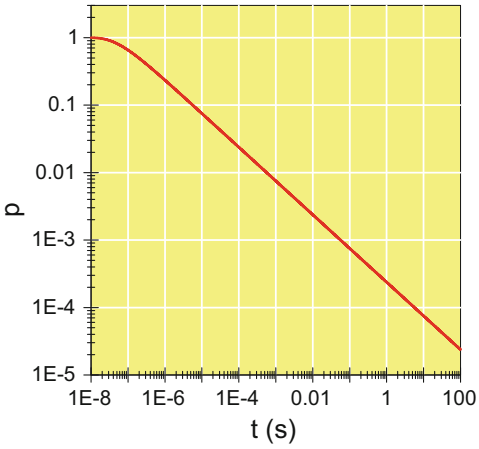

Fig. 8.10 Probability as a function of time to find the molecule at its initial adsorption site. Note the logarithmic scaling

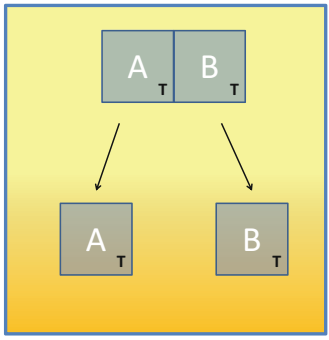

Fig. 8.11 Two systems A and B initially in contact at temperature T stay in equilibrium after their separation, where they can be considered decoupled

Problem 8.5 (continued)
system A is $p_A(E_A)$, the respective probability of measuring the energy E_B in system B is $p_B(E_B)$.

a. If the systems are separated from each other so that they can be considered decoupled, are they still in equilibrium and maintaining their initial temperature?
b. Write down an expression for the total energy E of both systems. If the systems are decoupled from each other, which condition follows for the probability $p(E)$ of measuring the total energy E?
c. Show that $p(E)$ is the Boltzmann distribution Eq. (8.3). *Hint: Set up a differential equation for the probability distribution.*

Solution 8.5 In this exercise, it is our goal to derive the Boltzmann distribution Eq. (8.3) for a system composed of two identical subsystems from very general

assumptions. Among the various derivations found in textbooks, this one is quite compact; thus, it can be reproduced in oral examinations. The two systems are initially in contact with each other and in equilibrium. The temperature in both subsystems is constant, but the energies E_A and E_B in the systems fluctuate around a mean value.

In **subproblem (a)**, we answer the question whether both systems stay in equilibrium if they are separated from each other. This is in fact the case. If two systems at different temperature are brought into contact, they equalize their temperature until equilibrium is established. If they are then decoupled, they maintain this temperature, at least if adhesion effects can be ignored. This idea, first introduced by J.W. Gibbs, guarantees the equilibrium of two perfectly decoupled systems at a constant temperature.

In **subproblem (b)**, we focus on the consequences of this situation: the total energy E is *additive*, i.e.,

$$E = E_\mathrm{A} + E_\mathrm{B}. \tag{8.47}$$

If the probability of finding an energy E_A in system A is $p_\mathrm{A}(E_\mathrm{A})$, and the probability of measuring E_B in system B is $p_\mathrm{B}(E_\mathrm{B})$, then we can set up a joint probability for the total system to measure the energy E. Because the systems are now independent of each other, the joint probability is obtained by multiplication of the probability distributions p_A and p_B:

$$p(E) = p_\mathrm{A}(E_\mathrm{A})\, p_\mathrm{B}(E_\mathrm{B}) \tag{8.48}$$

In **subproblem (c)**, we show that $p(E)$ is the Boltzmann distribution Eq. (8.3). In fact, the additivity of the energies in the subsystems (Eq. (8.47)) and their mutual independence (Eq. (8.48)) unambiguously determine the mathematical form of the probability distribution. But how can we show this? The first step may be the notion that the condition Eq. (8.48) is special, and that it is satisfied by the exponential function:

$$\mathrm{e}^{c\,E_a} \times \mathrm{e}^{c\,E_b} = \mathrm{e}^{c\,(E_a+E_b)} = \mathrm{e}^{c\,E}; \qquad c = \text{const.}$$

A second thought may be related to the property of a probability distribution function to be normalized. This requires $p_\mathrm{A}(E_\mathrm{A}) \to 0$ as $E_\mathrm{A} \to \infty$ and thus the gradient of $p_\mathrm{A}(E_\mathrm{A})$ to be negative. A good idea is to set up a differential equation for p_A. The starting point consists of the derivatives

$$\frac{\partial}{\partial E_\mathrm{A}} p(E) = \frac{\partial}{\partial E_\mathrm{A}} p_\mathrm{A}(E_\mathrm{A}) p_\mathrm{B}(E_\mathrm{B}) = p_\mathrm{B}(E_\mathrm{B}) \frac{\partial\, p_\mathrm{A}(E_\mathrm{A})}{\partial E_\mathrm{A}} \tag{8.49}$$

$$\frac{\partial}{\partial E_\mathrm{B}} p(E) = \frac{\partial}{\partial E_\mathrm{B}} p_\mathrm{A}(E_\mathrm{A}) p_\mathrm{B}(E_\mathrm{B}) = p_\mathrm{A}(E_\mathrm{A}) \frac{\partial\, p_\mathrm{B}(E_\mathrm{B})}{\partial E_\mathrm{B}} \tag{8.50}$$

on the one hand, and on the other hand

$$\frac{\partial}{\partial E_\mathrm{A}} p(E) = \frac{\partial p(E)}{\partial E} \underbrace{\frac{\partial E}{\partial E_\mathrm{A}}}_{=1} = \frac{\partial p(E)}{\partial E} \tag{8.51}$$

$$\frac{\partial}{\partial E_\mathrm{B}} p(E) = \frac{\partial p(E)}{\partial E} \underbrace{\frac{\partial E}{\partial E_\mathrm{B}}}_{=1} = \frac{\partial p(E)}{\partial E} \tag{8.52}$$

Division by $p(E)$ shows that these derivatives yield:

$$\frac{1}{p(E)} \frac{\partial p(E)}{\partial E} = \frac{1}{p_\mathrm{A}(E_\mathrm{A})} \frac{\partial p_\mathrm{A}(E_\mathrm{A})}{\partial E_\mathrm{A}} = \frac{1}{p_\mathrm{B}(E_\mathrm{B})} \frac{\partial p_\mathrm{B}(E_\mathrm{B})}{\partial E_\mathrm{B}} \tag{8.53}$$

Note that this condition holds for arbitrary E_A and E_B. As a consequence, these expressions must be constant. Because p_A, p_B and p are probability densities, they must be positive. Their gradients, as mentioned above, should be negative. Therefore, the constant must be a negative number:

$$\frac{1}{p(E)} \frac{\partial p(E)}{\partial E} = \frac{1}{p_\mathrm{A}(E_\mathrm{A})} \frac{\partial p_\mathrm{A}(E_\mathrm{A})}{\partial E_\mathrm{A}} = \frac{1}{p_\mathrm{B}(E_\mathrm{B})} \frac{\partial p_\mathrm{B}(E_\mathrm{B})}{\partial E_\mathrm{B}} = -\beta; \quad \beta > 0 \tag{8.54}$$

The differential equation, e.g., for p_A is obtained by rearrangement of this expression:

$$\frac{\partial p(E)}{\partial E} + \beta p_\mathrm{A}(E_\mathrm{A}) = 0 \tag{8.55}$$

Its solution is:

$$p_\mathrm{A}(E_\mathrm{A}) = C\mathrm{e}^{-\beta E_\mathrm{A}} \tag{8.56}$$

which is the Boltzmann distribution. The constant C must follow from the normalization of the distribution function. Its determination would require further assumptions about the nature of the system, e.g. if the spectrum of possible energy values is continuous or if it is discrete. C is closely related to the partition function. The assignment of β to the temperature of the system is achieved by comparison with a concrete case, e.g., the Maxwell-Boltzmann velocity distribution of a monatomic perfect gas. In this case, the average energy is $\frac{3}{2} k_B T$ (see Eq. (7.18) in Problem 7.1). By comparison, it can be shown that $\beta = \frac{1}{k_B T}$.

Problem 8.6 (Entropy of Monatomic Gases)

a. Prove that the molar entropy of a monatomic perfect gas with mass m and volume V is:

$$s = R \ln \left[\frac{(2\pi m k_B T)^{\frac{3}{2}}}{h^3} \frac{V}{N_A} \right] + \frac{5}{2} R \tag{8.57}$$

b. Calculate the standard molar entropies of gaseous neon, gaseous zinc, and gaseous lithium at $T = 298.15\,\mathrm{K}$. Compare the results with experimental values $s^{\ominus}(\mathrm{Ne(g)}) = 146.3\,\mathrm{J\,mol^{-1}\,K^{-1}}$, $s^{\ominus}(\mathrm{Zn(g)}) = 161.0\,\mathrm{J\,mol^{-1}\,K^{-1}}$, and $s^{\ominus}(\mathrm{Li(g)}) = 138.8\,\mathrm{J\,mol^{-1}\,K^{-1}}$.

Solution 8.6 Is statistical thermodynamics able to correctly predict the molar entropy of a monatomic gas? In this exercise, we analyze this in more detail. In **subproblem (a)**, we show that the molar entropy of a monatomic perfect gas is given by Eq. (8.57), which is called a *Sackur-Tetrode* equation in the literature. It is obvious that our starting point for calculating the entropy is Eq. (8.8)

$$S = \left(\frac{d}{dT} (k_B T \ln Q) \right)_{V,T}$$

which traces back the entropy to the system partition function, Q. The partition function in turn can be written as a product of the N single particle partition functions, where N is the number of particles, q. In our case $N = N_A$. The proper form of the latter is that of *indistinguishable particles* (see Eq. (8.6)); thus, the expression for the molar entropy becomes

$$s = \frac{d}{dT} \left(k_B T \ln \frac{1}{N_A!} q^{N_A} \right) = \frac{d}{dT} (N_A k_B T \ln q - k_B T \ln N_A!) \tag{8.58}$$

Next, we apply Stirling's approximation for the factorial $N_A! = N_A \ln N_A - N_A$ (see Eq. (A.62)) and we use the product rule Eq. (A.15) to form the derivative with regard to temperature:

$$s = N_A k_B \ln q + N_A k_B T \frac{d \ln q}{dT} - N_A k_B \ln N_A + N_A k_B \tag{8.59}$$

By means of Eq. (A.23) and $N_A k_B = R$, this can be transformed to

$$s = R \ln \frac{q}{N_A} + RT \frac{1}{q} \frac{dq}{dT} + R \tag{8.60}$$

Now, we must make an explicit assumption about the single particle partition function: a monatomic particle has only three translational degrees of freedom. Its partition function is given in Eq. (8.12). In particular, we have:

$$q = q_{\text{trans.}} = \frac{(2\pi m k_B T)^{\frac{3}{2}}}{h^3} V \tag{8.61}$$

and

$$\frac{1}{q}\frac{dq}{dT} = \frac{h^3}{(2\pi m k_B)^{\frac{3}{2}} V T^{\frac{3}{2}}} \frac{(2\pi m k_B)^{\frac{3}{2}} V^{\frac{3}{2}} T^{\frac{1}{2}}}{h^3} = \frac{3}{2T} \tag{8.62}$$

Insertion of these results into Eq. (8.60) yields the expression

$$s = R \ln \left[\frac{(2\pi m k_B)^{\frac{3}{2}}}{h^3} T^{\frac{3}{2}} \frac{V}{N_A} \right] + \frac{5}{2} R \tag{8.63}$$

which is equivalent to Eq. (8.57). A remarkable point is the occurrence of the Planck constant in the expression. This suggests that a quantum mechanical treatment of the gas might be necessary for the correct determination of the entropy.[8] Another remarkable point is that the only element-specific quantity in Eq. (8.57) is the particle mass. It is thus interesting to see how entropies calculated using the Sackur-Tetrode formula compare with experimental values for the standard molar entropies of monatomic gases.

In **subproblem (b)** we consider two examples, the rare gas neon, Ne(g), and zinc vapor, Zn(g). The atomic weights are $m_{\text{Ne}} = 20.18\, m_u$ and $m_{\text{Zn}} = 65.41\, m_u$ respectively. Assuming standard conditions and room temperature, the gas volume is:

$$V = 1\,\text{mol} \times \frac{RT}{p^{\ominus}} = 2.479 \times 10^{-2}\,\text{m}^3. \tag{8.64}$$

By taking the values h, k_B, N_A, and m_u from the appendix (Sect. A.1), we obtain the values shown in Table 8.1.

For neon and zinc, the agreement between calculated and experimental standard entropies is excellent. In the case of lithium, however, a deviation of more than $5\,\text{J}\,\text{K}^{-1}\,\text{mol}^{-1}$ is recognized. Can we understand and correct this discrepancy in detail? It is related to the internal degrees of freedom of the gas particles. The Sackur-Tetrode equation only takes into account the *translational* entropy of the gas, as we considered only the translational part of the partition function. Thus, we have overlooked one or more degrees of freedom, which are present in lithium,

[8] The calculation of the internal energy of the perfect gas based on Eq. (8.7) and the partition function Eq. (8.61) would in fact reproduce the classical result $U = \frac{3}{2}RT$.

Table 8.1 Standard molar entropies of monatomic gases at $T = 298.15\,\mathrm{K}$, calculated using the Sackur-Tetrode equation (8.57) in comparison with experimental values. All values in $\mathrm{J\,K^{-1}\,mol^{-1}}$

Element	$s^{\ominus}_{\mathrm{calc}}$	$s^{\ominus}_{\mathrm{exp}}$
Ne(g)	146.329	146.3
Zn(g)	160.995	161.0
Li(g)	133.017	138.8

but apparently not in zinc or in xenon: we need to consider the electronic structure of these particles. Lithium (atomic number $Z = 3$) has the electron configuration $1s^2\,2s^1$. Its electronic ground state is characterized by the term symbol ${}^2S_{\frac{1}{2}}$. The superscript "2" is the *multiplicity* of the electronic state.[9] The electronic partition function is obtained from Eq. (8.11), where the degeneracy g_i of the ith electronic state is given by its multiplicity $2S_i + 1$ with S_i being the total electronic spin in this state:

$$q_{\mathrm{el.}} = \sum_i (2S_i + 1)\,\mathrm{e}^{-\frac{E_i}{k_B T}} \tag{8.65}$$

The first excited electronic states of lithium have the term symbols ${}^2P_{\frac{1}{2}}$ and ${}^2P_{\frac{3}{2}}$. Their energy measured relative to the ground state energy is $178.5\,\mathrm{kJ\,mol^{-1}}$. As a consequence, these states are not occupied under room temperature conditions. They are thus negligible for the calculation of $q_{\mathrm{el.}}$. By taking $E_0 = 0$,

$$q_{\mathrm{el.}} = 2S_0 + 1 = 2, \tag{8.66}$$

and thus

$$q = q_{\mathrm{trans.}} q_{\mathrm{el.}} = 2\frac{(2\pi m k_B T)^{\frac{3}{2}}}{h^3} V. \tag{8.67}$$

This modification leads to a contribution to the entropy of $R\ln 2 = 5.763\,\mathrm{J\,K^{-1}\,mol^{-1}}$. The corrected value for the standard room temperature entropy of lithium is thus $138.780\,\mathrm{J\,K^{-1}\,mol^{-1}}$, in good agreement with the experimental value in Table 8.1. The ground states of atomic zinc and neon both have the term symbols ${}^1S_0$. There is thus no significant contribution of the electronic degrees of freedom to their room temperature entropy. Note that contributions resulting from the nuclear spin multiplicity and mixing of different isotopes are not included in the experimental value of the standard molar entropy. This is consistent with the third law of thermodynamics, i.e., the statement that $s^{\ominus}(T = 0\,\mathrm{K})$ of an element in

[9] The multiplicity $2S + 1$ of an electronic state is related to the total electronic spin S, which is determined in the case of the ground state by the single electron in the $2s$ atomic orbital. The electronic structure of lithium is treated in more detail in Problem 9.5.

the state of ideal crystallization is zero [4]. In summary, we see that statistical thermodynamics is able to predict the molar entropies of monatomic gases with remarkably good agreement. We have also seen how internal degrees of freedom of the gas particles contribute to the entropy.

Problem 8.7 (Heat Capacity of Multilevel Systems) Consider a system with the energy levels E_i and degeneracies g_i, $i = 1, \ldots, L$.

a. Prove that the constant volume molar heat capacity of the system can be written:

$$c_V(T) = R \frac{\sum_i^L \sum_j^L g_i g_j \frac{E_i^2 - E_i E_j}{k_B^2 T^2} \mathrm{e}^{-\frac{E_i + E_j}{k_B T}}}{\sum_i^L \sum_j^L g_i g_j \mathrm{e}^{-\frac{E_i + E_j}{k_B T}}} \tag{8.68}$$

b. Apply Eq. (8.68) to the rotational contribution to the heat capacity of molecular hydrogen, $H_2(g)$. The energy levels are given by (see Eq. (10.11) in Chap. 10):

$$E_J = \frac{h^2}{8\pi^2 I} J(J+1) \tag{8.69}$$

where J is the rotational quantum number and $I = 4.6 \times 10^{-48}\,\mathrm{kg\,m^2}$ is the molecule's moment of inertia. If nuclear spin symmetry is ignored, J can take even and odd values $J = 0, 1, 2, \ldots$ and a given rotational state is $(2J+1)$-fold degenerate. Plot $c_V(T)$ in the range between 0 and 500 K. Use at least ten rotational levels for your calculation. Interpret the behavior of $c_V(T)$ in the limit $T \to 0$ and $T \to \infty$. Can you explain the *overshooting* of the heat capacity in the temperature range between 50 and 100 K?

c. Molecular hydrogen is a mixture of ortho-H_2 and para-H_2. The ortho species is characterized by a total nuclear spin of $I = 1$ (multiplicity 3) and allows only odd rotational states, i.e., $J = 1, 3, 5 \ldots$. The para species combines a total nuclear spin of $I = 0$ (multiplicity 1) with even rotational states $J = 0, 2, 4 \ldots$. Plot the rotational contribution to the molar heat capacity of ortho and para hydrogen in the range between 0 and 500 K and comment on the differences.

Solution 8.7 In this problem, we deal with the rotational degrees of freedom of the diatomic molecule H_2 and how they contribute to its molar heat capacity. Historically, the correct interpretation of the low temperature molar heat capacity of molecular hydrogen was a problem that stimulated the development of early quantum mechanics [5]. The evaluation of the rotational contribution to the constant

volume molar heat capacity is based on the rotational partition function, q_{rot}. For the latter, however, no closed expression can be given, as in the case of the translational partition function or the harmonic oscillator vibrational partition function. Thus, we must fall back on Eq. (8.11).

In **subproblem (a)**, we show that Eq. (8.68) is the correct expression for the molar heat capacity of a system with L discrete energy levels E_i with a degree of degeneracy g_i respectively. We assume N indistinguishable subunits. Using Eq. (8.6), we have:

$$Q = \frac{1}{N!} q^N \tag{8.70}$$

where q is the partition function of an ensemble subunit, e.g., a single molecule. The internal energy is obtained from Eq. (8.7), i.e.,

$$U = -\left(\frac{\partial \ln Q}{\partial \beta}\right)_{T,V} = -\frac{\partial}{\partial \beta}\left(\ln \frac{q^N}{N!}\right) \tag{8.71}$$

where $\beta = \frac{1}{k_B T}$. Using Stirling's formula Eq. (A.62), we obtain:

$$U = -\frac{\partial}{\partial \beta}\left[N \ln\left(\sum_i^L g_i \mathrm{e}^{-\beta E_i}\right) - N \ln N + N\right]. \tag{8.72}$$

Then, application of the chain rule (Eq. (A.17)) yields

$$U = N \frac{\sum_i^L g_i E_i \mathrm{e}^{-\beta E_i}}{\sum_i^L g_i \mathrm{e}^{-\beta E_i}} \tag{8.73}$$

as the proper expression for the internal energy. The constant volume heat capacity for N particles is the derivative with regard to temperature:

$$C_V(T) = \left(\frac{\partial U}{\partial T}\right) = N \frac{\partial}{\partial T}\left(\frac{\sum_i^L g_i E_i \mathrm{e}^{-\frac{E_i}{k_B T}}}{\sum_i^L g_i \mathrm{e}^{-\frac{E_i}{k_B T}}}\right) \tag{8.74}$$

We must apply the product rule for differentiation in combination with the chain rule to obtain:

$$C_V(T) = N \left(\frac{\sum_i^L g_i E_i \mathrm{e}^{-\frac{E_i}{k_B T}} \left(\frac{E_i}{k_B T^2}\right)}{\sum_i^L g_i \mathrm{e}^{-\frac{E_i}{k_B T}}} - \frac{\sum_i^L g_i E_i \mathrm{e}^{-\frac{E_i}{k_B T}} \sum_j^L g_j \mathrm{e}^{-\frac{E_j}{k_B T}} \left(\frac{E_j}{k_B T^2}\right)}{\left(\sum_i^L g_i \mathrm{e}^{-\frac{E_i}{k_B T}}\right)^2} \right) \tag{8.75}$$

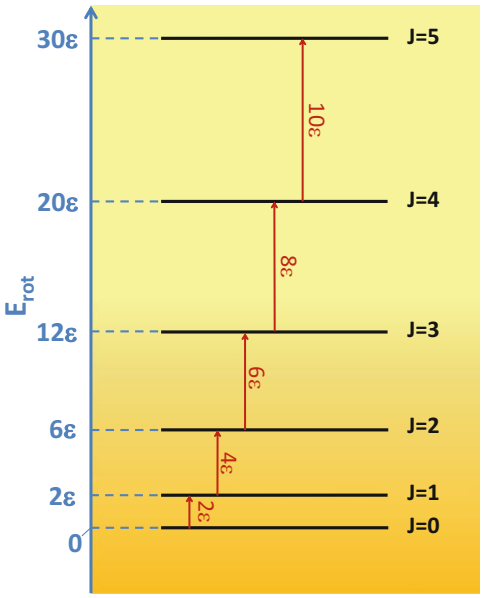

Fig. 8.12 Rotational energy levels of the H_2 molecule in the model of the rigid rotator (schematic). Rotational energies are multiples of $\epsilon = \frac{h^2}{8\pi^2 I}$ where I is the molecule's moment of inertia

In fact, we can write this in a more symmetrical way by reducing the terms to a common denominator, but we have to pay attention to the correct indexing:

$$C_V(T) = N \frac{\sum_i^L \sum_j^L g_i g_j E_i \left(\frac{E_i}{k_B T^2}\right) \mathrm{e}^{-\frac{E_i+E_j}{k_B T}} - \sum_i^L \sum_j^L E_i \left(\frac{E_j}{k_B T^2}\right) \mathrm{e}^{-\frac{E_i+E_j}{k_B T}}}{\sum_i^L \sum_j^L g_i g_j \mathrm{e}^{-\frac{E_i+E_j}{k_B T}}} \tag{8.76}$$

If we now factor out k_B from the numerator and assume that the particle number is Avogadro's number N_A, we obtain the molar heat capacity

$$c_v(T) = \underbrace{N_A k_B}_{R} \frac{\sum_i^L \sum_j^L g_i g_j \left(\frac{E_i^2 - E_i E_j}{k_B^2 T^2}\right) \mathrm{e}^{-\frac{E_i+E_j}{k_B T}}}{\sum_i^L \sum_j^L g_i g_j \mathrm{e}^{-\frac{E_i+E_j}{k_B T}}} \tag{8.77}$$

which is identical to the expression Eq. (8.68).

In **subproblem (b)**, we apply this to the concrete case of a rotating diatomic molecule H_2 if the effects of nuclear spin symmetry on the molecular rotation are ignored. The quantum mechanical model of molecular rotation is the rigid rotator, which is described in detail in Sect. 10.1.2. The rotational energy levels depend on the molecule's moment of inertia I and on the rotational quantum number J. According to Eq. (8.69), the energy levels are not equidistant, as can be seen in Fig. 8.12.

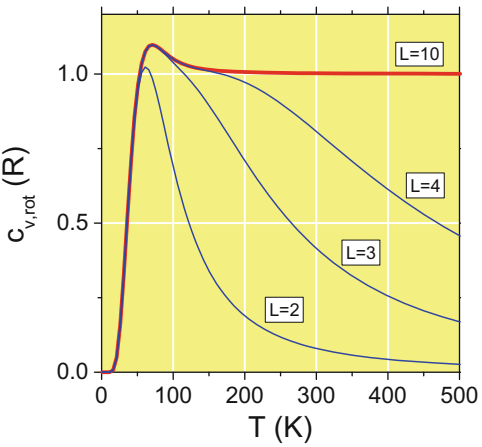

Fig. 8.13 Rotational contribution to the low temperature heat capacity of H_2 by ignoring nuclear spin symmetry, based on Eq. (8.68), with consideration of different numbers of rotational levels L. $c_{V,\mathrm{rot}}$ is plotted in units of the gas constant R

If we define $\epsilon = \frac{h^2}{8\pi^2 I} = 1.21 \times 10^{-21}$ J, then the energy levels and the distance between neighboring energy levels are multiples of ϵ. These distances become greater with increasing J (we refer to this point below). In addition, the rigid rotator energies have a degree of degeneracy of $g_i = (2J + 1)$. With this information, we can calculate the rotational contribution to the low temperature heat capacity using Eq. (8.68) and mathematical software. The result is shown in Fig. 8.13.

If at least $L = 10$ levels are considered, the heat capacity follows the bold line. At $T = 0$ K, the heat capacity is zero. Then, between 20 and 50 K it increases steeply and reaches a maximum at about 70 K. Above this temperature, the molar heat capacity decreases gradually toward a saturation value of $1R$. This high temperature limit is the classical value for two rotational degrees of freedom of the molecule contributing $\frac{1}{2}R$ to c_V. The fact that $c_{V,\mathrm{rot}} \to 0$ for $T \to 0$ shows that the rotational degrees of freedom are frozen at a very low temperature, where only the rotational level $J = 0$ is occupied. It is instructive to analyze the *overshooting* of the molar heat capacity exceeding the classical value of $1R$ by about 10% at about 70 K. The characteristics of $c_{V,\mathrm{rot}}$ in the case of a two-level system ($L = 2$) is also shown in Fig. 8.13. The steep increase above 20 K is caused by the population of the $J = 1$ level. Because the population of this excited state reaches a state of saturation at a higher temperature, the system can no longer absorb further energy; thus, the heat capacity decreases. If three levels are considered ($L = 3$), the peak in the heat capacity curve is well reproduced. The overshooting is thus caused by the population of the levels $J = 1$ and $J = 2$. The decrease in the heat capacity appears to be a consequence of the fact that the level $J = 3$ has too much in energy to be reached below 100 K.

Although a similar trend in the rotational molar heat capacity is observed in deuterated hydrogen (HD), ordinary H_2 shows a different behavior. As proposed for the first time in 1929 by Bonhoeffer and Harteck [6], H_2 has two spin-isomers, ortho-H_2 with a total nuclear spin of $I = 1$ (multiplicity 3) and para-H_2 with a total nuclear spin of $I = 0$ (multiplicity 1). Nuclear spin symmetry and the Pauli principle

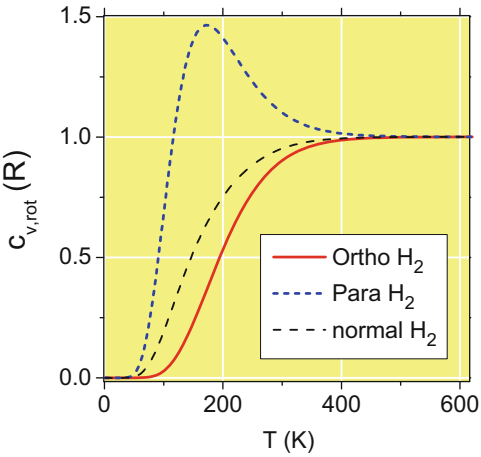

Fig. 8.14 Rotational contribution to the low temperature heat capacity of ortho H_2 (*solid*) and para H_2 (*short dashed*) based on Eq. (8.68). Also shown (*dashed*) is the curve for normal H_2, i.e., a mixture of ortho and para H_2 3:1. $c_{V,\mathrm{rot}}$ is plotted in units of the gas constant R

state that ortho-H_2 can only occupy the rotational states with odd J, whereas para-H_2 populates only states with even J.

In **subproblem (c)** we determine $c_{V,\mathrm{rot}}(T)$ in the region between 0 and 500 K for these two species. It is worth mentioning that a direct transition between these two species is forbidden. With

$$g_J^{\mathrm{ortho}} = 3(2J+1) \qquad g_J^{\mathrm{para}} = 2J+1 \tag{8.78}$$

and the restriction concerning the possible occupation of rotational states, the curves shown in Fig. 8.14 are obtained. The molar heat capacity of the para species increases considerably at temperatures above 50 K and overshoots the classical value $1R$ by nearly 50%. Above 170 K it decreases and approaches the classical limit. The function for ortho species, in contrast, continuously increases at temperatures above 100 K and approaches the classical limit. Normal H_2, i.e., a mixture of ortho and para hydrogen with the composition 3:1 also does not exhibit a heat capacity maximum. Looking back on our results, we have worked out the relation between the partition function and the molar heat capacity of a system of indistinguishable particles with a finite number of discrete energy levels. We have applied the method to the rotational contribution to the molar heat capacity of molecular hydrogen.

Problem 8.8 (Schottky Anomaly) Two-level systems exhibit a peak-shaped contribution to the molar heat capacity, known as Schottky anomaly.

a. Use Eq. (8.68) in Problem 8.7 and show that the contribution to the molar heat capacity of a two-level system is

(continued)

Problem 8.8 (continued)

$$c_{\text{Schottky}}(T) = R\left(\frac{\Delta}{k_B T}\right)^2 \frac{e^{\frac{\Delta}{k_B T}}}{\left(1 + e^{\frac{\Delta}{k_B T}}\right)^2} \tag{8.79}$$

where Δ is the energy difference between the two levels without degeneracy.

b. Show that $c_{\text{Schottky}}(T)$ has a peak value near

$$T_{\text{Peak}} \approx \frac{\Delta}{2.4\, k_B}. \tag{8.80}$$

Lithium doped potassium chloride, Li:KCl, exhibits a Schottky anomaly with a peak value near 0.4 K. Determine the energy difference Δ. Can you give an interpretation of the peak in the heat capacity vs temperature curve?

Solution 8.8 The appearance of a peak in the heat capacity vs temperature curves of materials is associated with the term Schottky anomaly. It appears, for example, in paramagnetic materials, but also in crystals of the alkali halide KCl, which are doped with the smaller lithium ion. The multilevel nature of this system is discussed in detail in Problem 9.17. In **subproblem (a)**, we lead back to Eq. (8.79), describing the heat capacity of a two-level system for the more general expressions for multilevel systems found in Problem 8.7. For $L = 2$ and $g_i = 1$, $i = 1, 2$ we can write:

$$c_{\text{Schottky}}(T) = R\frac{\frac{E_1^2 - E_1E_2}{k_B^2T^2}\mathrm{e}^{-\frac{E_1+E_2}{k_BT}} + \frac{E_2^2 - E_1E_2}{k_B^2T^2}\mathrm{e}^{-\frac{E_2+E_1}{k_BT}}}{\mathrm{e}^{-\frac{2E_1}{k_BT}} + 2\mathrm{e}^{-\frac{E_1+E_2}{k_BT}} + \mathrm{e}^{-\frac{2E_2}{k_BT}}} \tag{8.81}$$

Introducing the energy difference Δ between the two levels, we can make the substitution $E_2 = E_1 + \Delta$ and obtain

$$\begin{aligned} c_{\text{Schottky}}(T) &= R\frac{\frac{-E_1\Delta}{k_B^2T^2}\mathrm{e}^{-\frac{2E_1+\Delta}{k_BT}} + \frac{\Delta^2+E_1\Delta}{k_B^2T^2}\mathrm{e}^{-\frac{\Delta+2E_1}{k_BT}}}{\mathrm{e}^{-\frac{2E_1}{k_BT}} + 2\mathrm{e}^{-\frac{\Delta+2E_1}{k_BT}} + \mathrm{e}^{-\frac{2E_1+2\Delta}{k_BT}}} \\ &= R\frac{\frac{\Delta^2}{k_B^2T^2}\mathrm{e}^{-\frac{\Delta}{k_BT}}\mathrm{e}^{-\frac{2E_1}{k_BT}}}{\mathrm{e}^{-\frac{2E_1}{k_BT}} + 2\mathrm{e}^{-\frac{\Delta}{k_BT}}\mathrm{e}^{-\frac{2E_1}{k_BT}} + \mathrm{e}^{-\frac{2\Delta}{k_BT}}\mathrm{e}^{-\frac{2E_1}{k_BT}}} \\ &= R\frac{\frac{\Delta^2}{k_B^2T^2}\mathrm{e}^{-\frac{\Delta}{k_BT}}}{1 + 2\mathrm{e}^{-\frac{\Delta}{k_BT}} + \mathrm{e}^{-\frac{2\Delta}{k_BT}}} \end{aligned} \tag{8.82}$$

If we expand numerator and denominator by a factor $e^{\frac{2\Delta}{k_B T}}$ and apply the first binomial formula (Eq. (A.1)) to the denominator, we obtain the sought Eq. (8.79).

In **subproblem (b)**, we are interested in the position of the peak in the heat capacity vs temperature curve. We show that the peak temperature, T_{Peak}, is related to the splitting between the two levels according to Eq. (8.80). The trick is to introduce the dimensionless parameter $\alpha = \frac{\Delta}{k_B T}$. The heat capacity of the two-level system can be written as a function of α only:

$$c_{\text{Schottky}}(\alpha) = R \frac{\alpha^2 e^{\alpha}}{(1 + e^{\alpha})^2} \tag{8.83}$$

Extrema of the heat capacity will thus be characterized by a special value of α_m. The necessary condition for the maximum in the heat capacity vs temperature curve is:

$$\frac{d}{d\alpha} c_{\text{Schottky}}(\alpha) = \frac{d}{d\alpha} \frac{R\alpha^2 e^{\alpha}}{(1 + e^{\alpha})^2} \stackrel{!}{=} 0; \qquad \alpha = \alpha_m \tag{8.84}$$

Application of the product rule for differentiation (Eq. (A.15)) yields:

$$\frac{2\alpha e^{\alpha} + \alpha^2 e^{\alpha}}{(1 + e^{\alpha})^2} - \frac{2\alpha^2 e^{2\alpha}}{(1 + e^{\alpha})^3} = 0; \qquad \alpha = \alpha_m \tag{8.85}$$

Additional simplifications yield a transcendental equation:

$$e^{\alpha_m} = \frac{2 + \alpha_m}{\alpha_m - 2} \tag{8.86}$$

or

$$\alpha_m = \ln \frac{2 + \alpha_m}{\alpha_m - 2} \tag{8.87}$$

which cannot be further simplified. A graphical solution of the last equation is shown in Fig. 8.15, according to which the extremum is characterized by $\alpha_m = 2.3994 \approx 2.4$. We have thus justified Eq. (8.80). In **subproblem (c)**, we deal with the example of lithium doped KCl. Low-temperature measurements of the heat capacity show that this material exhibits a Schottky anomaly with a peak temperature of only $T_{\text{Peak}} \approx 0.4\,\text{K}$. This corresponds to a small energy splitting of:

$$\Delta = 2.4 k_B T_{\text{Peak}} = 1.3 \times 10^{-23}\,\text{J} = 8.3 \times 10^{-5}\,\text{eV}. \tag{8.88}$$

Below, in Problem 9.17, we deal with a simplified model of the Li:KCl system using quantum mechanics.

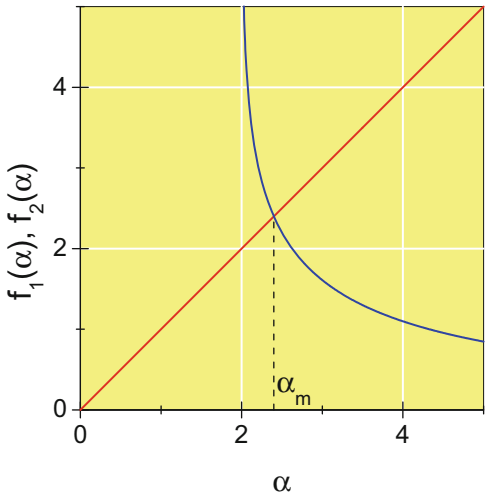

Fig. 8.15 Graphical solution of the transcendental equation (8.87). Function $f_1(\alpha) = \alpha$ is a line through the origin, function $f_2(\alpha) = \ln \frac{2+\alpha}{\alpha-2}$. The intersection of f_1 and f_2 is at $\alpha_m = 2.3994$

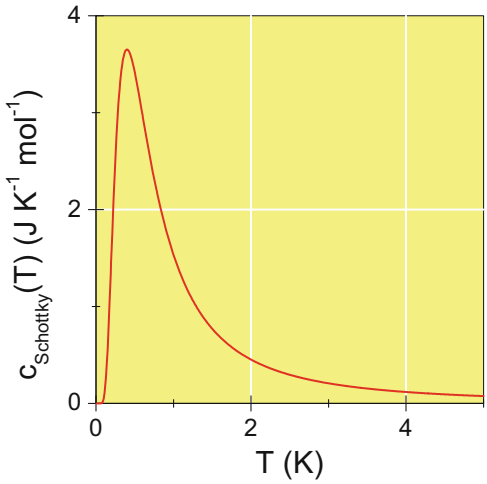

Fig. 8.16 Schottky anomaly in the system Li:KCl according to Eq. (8.79)

The heat capacity vs temperature curve of the Schottky anomaly in Li:KCl is shown in Fig. 8.16. Can we associate the peak temperature with a special condition of the two-level system? To analyze this, we consider the occupation probabilities of the two levels. Using the Boltzmann statistics Eq. (8.3), the latter can be expressed in terms of the parameter α:

$$p_1 = \frac{e^{-\frac{E_1}{k_B T}}}{e^{-\frac{E_1}{k_B T}} + e^{-\frac{E_2}{k_B T}}} = \frac{1}{1 + e^{-\frac{\Delta}{k_B T}}} = \frac{1}{1 + e^{-\alpha}} \tag{8.89}$$

$$p_2 = 1 - p_1 = \frac{e^{-\alpha}}{1 + e^{-\alpha}} \tag{8.90}$$

Let us consider the *change* in the occupation probability of the ground state:

$$\frac{\partial p_1}{\partial T} = \frac{\partial p_1}{\partial \alpha}\frac{\partial \alpha}{\partial T} = \frac{\mathrm{e}^{-\alpha}}{(1+\mathrm{e}^{-\alpha})^2}\left(-\frac{\Delta}{k_B T^2}\right) = -\frac{\Delta}{k_B T^2}\frac{\mathrm{e}^{-\frac{\Delta}{k_B T}}}{(1+\mathrm{e}^{-\frac{\Delta}{k_B T}})^2} \tag{8.91}$$

From Eq. (8.83) we obtain:

$$c_{\mathrm{Schottky}}(T) = N_A k_B \frac{\Delta^2}{k_B^2 T^2}\frac{\mathrm{e}^{-\frac{\Delta}{k_B T}}}{(1+\mathrm{e}^{-\frac{\Delta}{k_B T}})^2} \tag{8.92}$$

As a consequence, the change in occupation probability of the ground state is proportional to $c_{\mathrm{Schottky}}(T)$:

$$\frac{\partial p_1}{\partial T} = -\frac{1}{N_A \Delta} c_{\mathrm{Schottky}}(T) \tag{8.93}$$

Therefore, the peak in the heat capacity can be associated with the maximum decrease in occupation probability of the ground state. Obviously, because of Eq. (8.90) and thus

$$\frac{\partial p_2}{\partial T} = -\frac{\partial p_1}{\partial T}, \tag{8.94}$$

the population gain of level 2 also reaches a maximum at the peak temperature T_{Peak}. The change in occupation probability of the excited state as a function of temperature is also shown in Fig. 8.17.

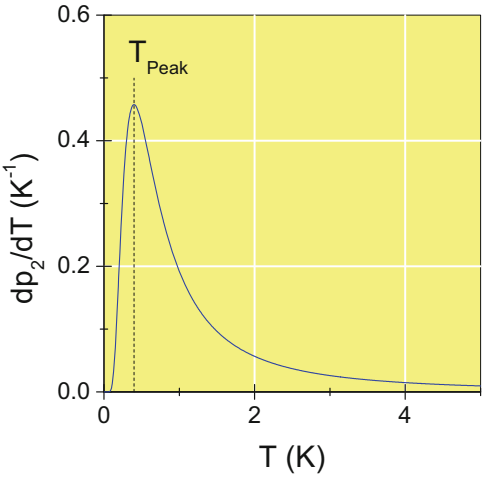

Fig. 8.17 Population change of the excited state in the two-level system related to the Schottky anomaly in Li:KCl. The maximum gain of p_2 is found at the peak temperature T_{Peak} (Eq. (8.80))

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