

17.E: Boltzmann Factor and Partition Functions (Exercises)

A Libretexts Textmap organized around McQuarrie and Simon's textbook

Physical Chemistry: A Molecular Approach

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These are homework exercises to accompany [Chapter 17](#) of McQuarrie and Simon's "Physical Chemistry: A Molecular Approach" Textmap.

Q17.9

In Section 17-3, we derived an expression for the expectation value of energy, $\langle E \rangle$, by applying Equation 17.20 to $Q(N, V, T)$ given by Equation 17.22. Now, apply Equation 17.21 to $Q(N, V, T)$ to give the same result, except with β replaced by $\frac{1}{k_b T}$.

S17.9

Beginning with Equation 17.21

$$\langle E \rangle = k_b T^2 \left(\frac{\partial \ln Q}{\partial T} \right)_{N,V}$$

We can use the partition function in the problem to find $\left(\frac{\partial \ln Q}{\partial T} \right)_{N,V}$:

$$\begin{aligned} Q(N, V, T) &= \frac{V^N}{N!} \left(\frac{2\pi m k_b}{h^2} \right)^{\frac{3N}{2}} \frac{1}{T^{\frac{3N}{2}}} \\ \ln Q &= \frac{3N}{2} \ln T \\ \left(\frac{\partial \ln Q}{\partial T} \right)_{N,V} &= \frac{3N}{2T} \end{aligned}$$

Substituting this last result into Equation 17.21 yields

$$\langle E \rangle = k_b T^2 \frac{3N}{2T} = \frac{3}{2} (N k_b T)$$

Q17.10

A gas absorbed on a surface can sometimes be modeled as a two-dimensional ideal gas. We will learn in that the partition function of a two-dimensional ideal gas is:

$$Q(N, A, T) = \frac{1}{N!} \left(\frac{2\pi m k_B T}{h^2} \right)^N A^N \quad (17.E.1)$$

where A is the area of the surface. Derive an expression for \bar{C}_V .

S17.10

$$\bar{C}_V = \left(\frac{\partial U}{\partial T} \right)_{N,A} \text{ and } U = K_b T^2 \left(\frac{\partial \ln(Q)}{\partial T} \right)_{N,A}$$

Addition:

$$\bar{C}_V = \left(\frac{\partial U}{\partial T} \right)_{N,A}$$

and

$$U = K_b T^2 \left(\frac{\partial \ln(Q)}{\partial T} \right)_{N,A}$$

where

$$U = K_b T^2 * \frac{N}{T}$$

and thus
 $U = NK_bT.$

Q17.11

Given the partition function of a monatomic van der Waals gas:

$$Q(N, V, T) = \frac{1}{N!} \left(\frac{2\pi mk_B T}{h^2} \right)^{\frac{3N}{2}} (V - Nb)^N e^{-\frac{aN^2}{Vk_B T}} \quad (17.E.2)$$

what is the average energy of this gas?

S17.11

The average energy of a gas is given by

$$\langle E \rangle = k_B T^2 \left(\frac{\partial \ln Q}{\partial T} \right)_{N, V} \quad (17.E.3)$$

taking the natural log of the partition function gives us

$$\ln Q = \frac{3N}{2} \ln \left(\frac{2\pi mk_B T}{h^2} \right) + \frac{aN^2}{Vk_B T} + \frac{1}{N!} N \ln(V - Nb) \quad (17.E.4)$$

Now we take the partial derivative with respect to T while holding N and V constant.

This yields

$$\left(\frac{\partial \ln Q}{\partial T} \right)_{N, V} = \frac{3N h^2 2\pi m k_b}{4\pi m k_b T} - \frac{aN^2}{Vk_b T^2} = \frac{3N}{2T} - \frac{aN^2}{Vk_b T^2} \quad (17.E.5)$$

Substituting this value into the Average Energy equation, we get

$$\langle E \rangle = \frac{3N k_b T}{2} - \frac{aN^2}{V} \quad (17.E.6)$$

Q17.12

Given the following equation:

$$Q(N, V, T) = \frac{(V)^N}{N!} \left(\frac{2\pi mk_B}{h^2} \right)^{\frac{3N}{2}} T^{\frac{3N}{2}} \quad (17.E.7)$$

An approximate partition function for a gas of hard spheres can be obtained from the partition function of a monatomic gas by replacing V in the given equation with $V - b$, where b is related to the volume of the N hard spheres. Derive expressions for the energy and the pressure of this system.

S17.12

We can use the partition function specified in the problem to find

$$Q(N, V, T) = \frac{(V - b)^N}{N!} \left(\frac{2\pi mk_B}{h^2} \right)^{\frac{3N}{2}} T^{\frac{3N}{2}} \quad (17.E.8)$$

$$\ln Q = \frac{3N}{2} \ln T + \text{terms not involving } T \quad (17.E.9)$$

After substitution into the given equation, we find that the energy (E) is the same as that for a monatomic ideal gas: $3Nk_B T/2$. We can use the partition function specified in the problem to find

$$Q(N, V, T) = \frac{1}{N!} \left(\frac{2\pi mk_B T}{h^2} \right)^{\frac{3N}{2}} (V - b)^N \quad (17.E.10)$$

$$\ln Q = N \ln(V - b) + \text{terms not involving } V \quad (17.E.11)$$

Similar substitution allows us to find

$$\langle P \rangle = k_B T \left(\frac{\partial \ln Q}{\partial V} \right)_{N, T} = \frac{N k_B T}{V - b} \quad (17.E.12)$$

Q17.13

Using the partition function

$$Q(N, A, T) = \frac{1}{N!} \left(\frac{2\pi m k_B T}{h^2} \right)^N A^N \quad (17.E.13)$$

calculate the heat capacity of a two-dimensional ideal gas.

S17.13

First, the energy must be found. This can be done by finding $\left(\frac{\partial \ln Q}{\partial T} \right)_{N, V}$.

$$\ln[Q] = N \ln[T] + \dots \quad (17.E.14)$$

where the ... refers to terms that do not depend on T. Because they do not depend on T, the partial with respect to those terms are 0.

The partial derivative is

$$\left(\frac{\partial \ln Q}{\partial T} \right)_{N, V} = \frac{N}{T} \quad (17.E.15)$$

The energy can be expressed as

$$E = \left(\frac{\partial \ln Q}{\partial T} \right)_{N, V} * k_B T^2 \quad (17.E.16)$$

$$E = \frac{N k_B T^2}{T} \quad (17.E.17)$$

$$E = N k_B T \quad (17.E.18)$$

In the case of our two-dimensional ideal gas,

$$E = U \quad (17.E.19)$$

so we can use the relationship

$$C_v = \left(\frac{\partial U}{\partial T} \right)_{N, V} \quad (17.E.20)$$

$$C_v = N k_B \quad (17.E.21)$$

Q17-14 This is correct, but show algebra for better understanding of the topic.

How is the energy of a monatomic van der Waals gas related to the capacity of a monatomic van der Waals gas?

S17-14

The heat capacity, C_v is a measure of how energy changes with temperature (given a constant amount and volume).

$$C_v = \left(\frac{\partial \langle E \rangle}{\partial T} \right)_{N, V} = \left(\frac{\partial U}{\partial T} \right)_{N, V} \quad (17.E.22)$$

because $\langle E \rangle = U$.

Q17.15

The partition function of the rigid rotator-harmonic oscillator model of an ideal diatomic gas is given by

$$Q(N, V, \beta) = \frac{[q(V, \beta)]^N}{N!} \quad (17.E.23)$$

where

$$q(V, \beta) = \left(\frac{2\pi m}{h^2 \beta} \right) \left(\frac{3}{2} \right) * V * \frac{8\pi^2 I}{h^2 \beta} * \frac{e^{(-\beta h \nu / 2)}}{1 - e^{(-\beta h \nu / 2)}} \quad (17.E.24)$$

Find the expression for the pressure of an ideal atomic gas.

S17.15

(There needs to be way more details how you arrived from the first equation to the last. -- RM)

$$Q(N, V, \beta) = \frac{1}{N!} \left(\frac{2\pi m}{h^2 \beta} \right)^N * V^N * \frac{8\pi^2 I^N}{h^2 \beta} * \frac{e^{(-\beta h \nu / 2)}}{1 - e^{(-\beta h \nu / 2)}}^N \quad (17.E.25)$$

$$\ln Q = N \ln V \quad (17.E.26)$$

$$\frac{d \ln Q}{dV} = \frac{N}{V} \quad (17.E.27)$$

$$\langle P \rangle = \frac{N k_B T}{V} \quad (17.E.28)$$

which is the ideal gas law.

It would be useful to show the intermediate step in how you got to the end solution...I feel that the more detail it is, the clearer the solution will be.

Q17.19

a.) Prove that a simplified form of the molar heat capacity of system of independent particles can be written as:

$$\overline{C_V} = R(\beta \varepsilon)^2 \frac{e^{-\beta \varepsilon}}{(1 + e^{-\beta \varepsilon})^2} \quad (17.E.29)$$

b.) Verify by plotting $\overline{C_V}$ versus $\beta \varepsilon$ that the maximum value occurs when $\beta \varepsilon = 2.40$.

S17.19

a.) We can write the partition function of the system as:

$$q = e^{-\frac{\varepsilon_0}{k_B T}} + e^{-\frac{\varepsilon_1}{k_B T}} \quad (17.E.30)$$

If we assume that the ground quantum state, ε_0 is equal to zero, we get:

$$q = e^{-\frac{0}{k_B T}} + e^{-\frac{\varepsilon_1}{k_B T}} = 1 + e^{-\frac{\varepsilon_1}{k_B T}} \quad (17.E.31)$$

We can then write the average energy of the system in terms of q:

$$\begin{aligned} \langle E \rangle &= RT^2 \left(\frac{\partial \ln(q)}{\partial T} \right)_V = RT^2 \left(\frac{\partial \ln \left(1 + e^{-\frac{\varepsilon_1}{k_B T}} \right)}{\partial T} \right)_V = RT^2 \frac{1}{1 + e^{-\frac{\varepsilon_1}{k_B T}}} \left(-\frac{\varepsilon_1}{k_B} \right) \left(-\frac{1}{T^2} \right) e^{-\frac{\varepsilon_1}{k_B T}} \\ &= R \left(\frac{\varepsilon_1}{k_B} \right) \frac{e^{-\frac{\varepsilon_1}{k_B T}}}{1 + e^{-\frac{\varepsilon_1}{k_B T}}} \end{aligned} \quad (17.E.32)$$

Using the definition of molar heat capacity, we can then plug in our expression for $\langle E \rangle$:

$$\overline{C_V} = \left(\frac{\partial \langle E \rangle}{\partial T} \right)_V = \left(\frac{\partial \left(R \left(\frac{\varepsilon_1}{k_B} \right) \frac{e^{-\frac{\varepsilon_1}{k_B T}}}{1 + e^{-\frac{\varepsilon_1}{k_B T}}} \right)}{\partial T} \right)_V \quad (17.E.33)$$

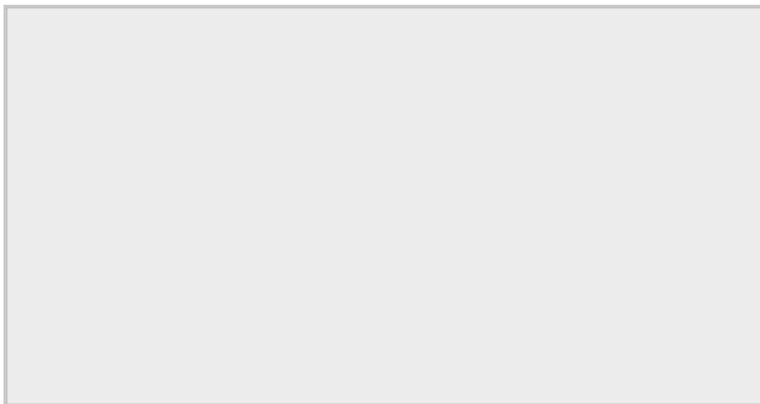
$$= R \left(\frac{\varepsilon_1}{k_B} \right) \left(-\frac{\varepsilon_1}{k_B} \right) \left(-\frac{1}{T^2} \right) e^{-\frac{\varepsilon_1}{k_B T}} \left(1 + e^{-\frac{\varepsilon_1}{k_B T}} \right)^{-2} = R \left(\frac{\varepsilon_1}{k_B T} \right)^2 \frac{e^{-\frac{\varepsilon_1}{k_B T}}}{\left(1 + e^{-\frac{\varepsilon_1}{k_B T}} \right)^2} \quad (17.E.34)$$

If we define $\varepsilon_1 = \varepsilon$ and $\frac{1}{k_B T} = \beta$, we can simplify the above expression for the molar heat capacity as:

$$\overline{C_V} = R(\beta\varepsilon)^2 \frac{e^{-\beta\varepsilon}}{(1 + e^{-\beta\varepsilon})^2} \quad (17.E.35)$$

which is what the original problem asked us to show.

b.) Plotting $\overline{C_V}$ versus $\beta\varepsilon$ results in the following graph, with the maximum at $\beta\varepsilon = 2.40$ verified. (All calculations and graphs were done in MATLAB and produced by me)



Q17.20

Each of the N atoms of the crystal is assumed to vibrate independently about its lattice position, so that the crystal is pictured as N independent harmonic oscillators, each vibrating in three directions. The partition function of a harmonic oscillator is

$$q_{ho}(T) = \sum_{\nu=0}^{\infty} e^{-\beta(\nu + \frac{1}{2})h\nu} \quad (17.E.36)$$

$$e^{-\beta h\nu/2} \sum_{\nu=0}^{\infty} e^{\beta \nu h\nu} \quad (17.E.37)$$

This summation is easy to evaluate if you recognize it as the so-called geometric series

$$\sum_{\nu=0}^{\infty} x^{\nu} = \frac{1}{1-x} \quad (17.E.38)$$

Show that

$$q_{ho}(T) = \frac{e^{-\beta h\nu/2}}{1 - e^{-\beta h\nu}} \quad (17.E.39)$$

and that

$$Q = e^{\beta U_0} \left(\frac{e^{-\beta h\nu/2}}{1 - e^{-\beta h\nu}} \right)^3 N \quad (17.E.40)$$

where U_0 simply represents the zero-of-energy, where all N atoms are infinitely separated.

S17.20

let $x = e^{-\beta h\nu}$ then $\sum_{\nu=0}^{\infty} e^{-\beta h\nu} = \frac{1}{1 - e^{-\beta h\nu}}$

$$Q = q^N = (q_{vib} q_{elec})^N$$

$$\{q_{\text{elec}}\} = e^{-\beta U_0 / N} + q_{\text{vib}} = (q_{\text{ho}})^3$$

$$Q = e^{-\beta U_0} \left(\frac{e^{-\beta h\nu/2}}{1 - e^{-\beta h\nu}} \right)^{3N} \quad (17.E.41)$$

Q17.21

Evaluate

$$S = \sum_{i=0}^2 \sum_{j=0}^1 x^{i+j} = x(1+y) + x^2(1+y) = (x+x^2)(1+y) \quad (17.E.42)$$

by summing over j first then over i. Now obtain the same result by writing S as a product of two separate summations.

S17.21

By evaluating the formula given in the problem, S can be written as a product of two separate summations, given by

$$S = \sum_{i=0}^2 \sum_{j=0}^1 = (x+x^2)(y+1) \quad (17.E.43)$$

Q17.22

Evaluate:

$$S = \sum_{i=0}^4 \sum_{j=1}^i 5+j \quad (17.E.44)$$

S17.22

$$(1+5) + [(1+5) + (2+5)] + [(1+5) + (2+5) + (3+5)] + [(1+5) + (2+5) + (3+5) + (4+5)] = 6 + 13 + 21 + 30 = 70 \quad (17.E.45)$$

Q17.24

Consider a system of two noninteracting identical fermions, each has energy states of ϵ_1 , ϵ_2 and ϵ_3 . How many terms are there in the unrestricted evaluation of $Q(2,V,T)$?

S17.24

$$Q(2,V,T) = \sum e^{-\beta(\epsilon_i + \epsilon_j)}$$

Total terms = 9. From these 9 terms that will appear in the unrestricted evaluation of Q, only 3 of them will be allowed for 2 identical fermions:

$$\epsilon_1 + \epsilon_2$$

$$\epsilon_1 + \epsilon_3$$

$$\epsilon_2 + \epsilon_3$$

The 6 terms that are not allowed by the fermion restriction would be (Aaron Choi):

$$\epsilon_1 + \epsilon_3 = \epsilon_3 + \epsilon_1 \quad (17.E.46)$$

$$\epsilon_1 + \epsilon_2 = \epsilon_2 + \epsilon_1 \quad (17.E.47)$$

$$\epsilon_2 + \epsilon_3 = \epsilon_3 + \epsilon_2 \quad (17.E.48)$$

Q17.25

Looking at problem 17.24, how many allowed terms are there in the case of bosons instead of fermions?

S17.25

There are six allowable terms, three that were found in Q17.24 and an additional three, they are as follows:

$$\epsilon_1 + \epsilon_3 \quad (17.E.49)$$

$$\epsilon_1 + \epsilon_2 \quad (17.E.50)$$

$$\epsilon_2 + \epsilon_3 \quad (17.E.51)$$

$$\epsilon_1 + \epsilon_1 \quad (17.E.52)$$

$$\epsilon_2 + \epsilon_2 \quad (17.E.53)$$

$$\epsilon_3 + \epsilon_3 \quad (17.E.54)$$

Q17.26

Consider a system of three noninteracting identical bosons, each of which has states with energies ϵ_1 , ϵ_2 , and ϵ_3 . How many terms are there in the unrestricted evaluation of $Q(3, V, T)$? How many terms occur in $Q(3, V, T)$ when the boson restriction is taken into account? Enumerate the allowed total energies in the summation of Equation 17.37:

$$Q(N, V, T) = \sum_{i,j,k..} e^{-\beta(\epsilon_i + \epsilon_j + \epsilon_k \dots)} \quad (17.E.55)$$

S17.26

There are ten allowed terms, given by the total energies

$$1. \epsilon_1 + \epsilon_2 + \epsilon_3 \quad (17.E.56)$$

$$2. \epsilon_1 + \epsilon_1 + \epsilon_3 \quad (17.E.57)$$

$$3. \epsilon_2 + \epsilon_2 + \epsilon_3 \quad (17.E.58)$$

$$4. \epsilon_2 + \epsilon_2 + \epsilon_1 \quad (17.E.59)$$

$$5. \epsilon_2 + \epsilon_2 + \epsilon_2 \quad (17.E.60)$$

$$6. \epsilon_2 + \epsilon_2 + \epsilon_3 \quad (17.E.61)$$

$$7. \epsilon_1 + \epsilon_3 + \epsilon_3 \quad (17.E.62)$$

$$8. \epsilon_3 + \epsilon_2 + \epsilon_3 \quad (17.E.63)$$

$$9. \epsilon_1 + \epsilon_1 + \epsilon_1 \quad (17.E.64)$$

$$10. \epsilon_3 + \epsilon_3 + \epsilon_3 \quad (17.E.65)$$

Q17.26

Consider a system of 2 noninteracting bosons, each having a state with energy $\epsilon_1, \epsilon_2, \epsilon_3, \epsilon_4$. How many terms are in the unrestricted evaluation $Q(2, V, T)$ Write the allowed energies in the summation form?.

S17.26

There are 10 allowed terms, given by the total energies

$$\epsilon_1 + \epsilon_2 \quad \epsilon_2 + \epsilon_2$$

$$\epsilon_1 + \epsilon_3 \quad \epsilon_2 + \epsilon_3$$

$$\epsilon_1 + \epsilon_4 \quad \epsilon_2 + \epsilon_4$$

$$\epsilon_1 + \epsilon_1 \quad \epsilon_3 + \epsilon_4$$

$$\epsilon_4 + \epsilon_4 \quad \epsilon_3 + \epsilon_3$$

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