Advanced Thermodynamics

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Chapter 1: The machinery of statistical thermodynamics

"A statistical model that can be derived exactly from the underlying microscopic interactions."

1.1 Outline and basic definitions

Statistical thermodynamics was developed by Maxwell, Boltzmann, Gibbs and Einstein between 1860 - 1905. In this course, we will address topics such as:

- What is the connection between the microscopic interactions of a system and classical thermodynamics?
- Where do the expressions, such as $U = \frac{3}{2}nRT$ or $H = \frac{5}{2}nRT$ for monatomic ideal gases, used in classical thermodynamics come from?
- What are the underlying approximations behind the ideal gas law $(PV = nRT)$?
- What is the statistical interpretation of entropy $(S = k\ln(\Omega))$?
- What are Maxwell-Boltzmann, Bose-Einstein, and Fermi-Dirac distributions?
- What is the origin of the most common equations of state for gases?
- Thermodynamics of molecules and thermochemistry

We will assume a large number of particles such that the system can be treated statistically. The underlying behavior of the individual particles (atoms/molecules) may be governed by classical or quantum mechanics (e.g., electronic, translational, rotational, vibrational energy).

Terminology:

System = Macroscopic thermodynamic system.
Particles = Particles that compose the system (e.g., atoms/molecules).
Macrostate = Macroscopic paramters (e.g., V, P, T) that specify the state of the system.
Microstate = Atom/molecular level specification of the system (e.g., positions and velocities of individual atoms/molecules).

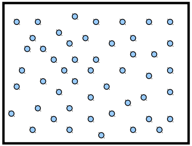
For a given macrostate many different microstates are possible. Usually only macrostate is observable.

Ensemble: A hypothetical collection of non-interacting systems. Each member has the same macrostate described by:

- (n, V, T) - Canonical ensemble. **We will employ this ensemble here.**
- (n, V, U) - Microcanonical ensemble.
- (μ, V, T) - Grand canonical ensemble.

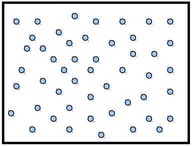
where n is the number of particles (no unit), V is the volume (m^{-3}), T is the temperature (K), U is the internal energy (J), and μ is the chemical potential (J). Although the ensemble members have an identical macrostate, they do not correspond to the same microstate.

The choice of n vs. μ often depends on whether a finite or a bulk system is considered. In general, a system can be described within any ensemble, but the actual calculations might be easier or more complicated depending on the choice.

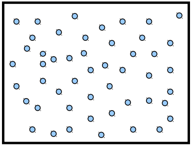


Microscopic view:
Individual atoms and molecules

Macroscopic view: homogeneous
distribution of atoms and molecules



Canonical ensemble member 1
Macroscopic *V*, *T*, *n* fixed



Canonical ensemble member 2
Macroscopic *V*, *T*, *n* fixed

Measurement: A measurement of any macroscopic property consists of a time average over the measurement interval. Hence it involves an inherent time averaging process. *How to avoid this?*

1.2 Boltzmann probability

Postulate: The measured time average of any macrosopic property of the system is equal to the average value of that property in the ensemble. This approach avoids taking time averages of the system (and hence considering the explicit microscopic level dynamics).

The internal energy (U) of a an ensemble is given by a weighted average of the ensemble members (*ensemble average*):

$$U = \langle E_i \rangle = \sum_{i=1}^{\infty} p_i E_i \tag{1.1}$$

where E_i is the energy of ensemble member i (J; includes a possible zero-point energy offset) and p_i is its statistical weight (probability of the member; no unit).

Since the available thermal energy dictates which ensemble members can be reached, we expect that p_i should depend on E_i. For example, an ensemble member that has a very high energy (as compared to the available thermal energy) would have a low probability of occurring (i.e., small p_i). Therefore it would not contribute much to the summation in Eq. (1.1).

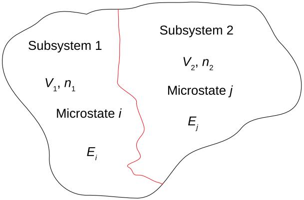
In the following, our task is to show that p_i is indeed determined by E_i:

$$p_i = \frac{e^{-\beta E_i}}{Z} \text{ where } Z = \sum_{i=1}^{\infty} e^{-\beta E_i} \tag{1.2}$$

Also, it will turn out that $\beta = \frac{1}{kT}$ (k is the Boltzmann constant).

Assumption: All microstates that have equal energy have the same probability of occurring. This implies that the probability depends only on energy: $p_i = f(E_i)$. Note that states that belong to the same degenerate set are counted separately.

Evaluation of Boltzmann probabilities p_i: Our task is to determine the function f above.



System = 1 + 2 in microstate $k = (i, j)$
$V = V_1 + V_2$, $n = n_1 + n_2$

We divide an ensemble member into two subsystems labelled by 1 and 2 in microstates i and j, respectively (see above). Based on the above assumption, we have:

$$p_{1,i} = f(E_{1,i}) \text{ and } p_{2,j} = g(E_{2,j}) \tag{1.3}$$

where $p_{1,i}$ is the probability for subsystem 1 in microstate i to occur and $p_{2,j}$ is the corresponding probability for subsystem 2 and microstate j.

Note that f and g are not necessarily the same functions (although they will turn out to be so).

Provided that the interaction energy between the two subsystems is small compared to the overall energies of the subsystems (e.g., n_1 and n_2 are large), the total energy of the system is given by:

$$E_{1+2,k} = E_{1,i} + E_{2,j} \text{ where } k = (i,j) \tag{1.4}$$

The probability for the system in microstate k is then:

$$p_{1+2,k} = h(E_{1+2,k}) \text{ where } k = (i,j) \tag{1.5}$$

Since the subsystems are indepdendent, the overall probability must be a product:

$$h(E_{1+2,k}) = h(E_{1,i} + E_{2,j}) = f(E_{1,i}) \times g(E_{2,j}) \tag{1.6}$$

Therefore we are therefore looking for a probability function, which produces a product from the sum of two energies (probably the exponential function!). To see this, we carry out the following calculation:

Denote $x \equiv E_{1,i}$, $y \equiv E_{2,j}$, and $z \equiv x + y$. With this notation, the above equation becomes:

$$h(z) = f(x)g(y) \tag{1.7}$$

Differentiating Eq. (1.7) with respect to x from both sides gives:

$$\left(\frac{\partial h(z)}{\partial x}\right)_y = \left(\frac{df(x)}{dx}\right) g(y) \tag{1.8}$$

Using the chain rule on the left-hand side gives:

$$\left(\frac{\partial h(z)}{\partial x}\right)_y = \left(\frac{dh(z)}{dz}\right)\left(\frac{\partial z}{\partial x}\right)_y = \frac{dh(z)}{dz} \tag{1.9}$$

Combining Eqs. (1.8) and (1.9) yields:

$$\frac{dh(z)}{dz} = \left(\frac{df(x)}{dx}\right) g(y) \tag{1.10}$$

Similarily, performing the same operation with respect y gives:

$$\frac{dh(z)}{dz} = f(x)\left(\frac{dg(y)}{dy}\right) \tag{1.11}$$

Dividing Eqs. (1.10) and (1.11) side by side ($dh(z)/dz$ cancels; ' denotes derivative) leads to:

$$\frac{g'(y)}{g(y)} = \frac{f'(x)}{f(x)} \equiv \beta \text{ (constant)} \tag{1.12}$$

Since the two sides in the first part of this equation depend on x and y independently, they must be equal to a constant (β).

Eq. (1.12) is a differential equation for f (or equivalently for g):

$$f'(x) = -\beta f(x) \Rightarrow f(x) = Ce^{-\beta x} \tag{1.13}$$

where C is the integration constant. Recalling that $x = E_{1,i}$ we can write this as:

$$p_{1,i} = f(E_{1,i}) = Ce^{-\beta E_{1,i}} \tag{1.14}$$

Since the same argument can be made for subsystem 2, β is a universal constant (that may depend on temperature).

When considering an ensemble (with $p_i = C\exp(-\beta E_i)$), the probabilities must be normalized to one:

$$\sum_{i=1}^{\infty} p_i = \sum_{i=1}^{\infty} Ce^{-\beta E_i} = 1 \tag{1.15}$$

This determines the integration constant C:

$$C = \frac{1}{\sum_{i=1}^{\infty} \exp(-\beta E_i)} \equiv \frac{1}{Z} \tag{1.16}$$

where Z is called the *partition function*. Although Z seems to play just the role of a normalization constant, it will turn out to be a central object in statistical thermodynamics (similar to the wavefunction in quantum mechanics). We conclude that the probabilities for ensemble members are given by:

$$p_i = \frac{e^{-\beta E_i}}{\sum_{j=1}^{\infty} e^{-\beta E_j}} = \frac{e^{-\beta E_i}}{Z} \tag{1.17}$$

1.3 Evaluation of internal energy

The internal energy U can be obtained as an ensemble average:

$$U(T) = \sum_{i=1}^{\infty} p_i E_i = \frac{1}{Z} \sum_{i=1}^{\infty} e^{-\beta E_i} \times E_i \tag{1.18}$$

where $Z = Z(\beta(T), V, n)$ and n may include several variables representing each species present in the system. Note that this choice of variables corresponds to *canonical ensemble* (i.e., fixed T, V, n).

Differentiation of $Z = \sum_{i=1}^{\infty} \exp\left(-\beta E_i\right)$ with respect to β gives:

$$\left(\frac{\partial Z}{\partial \beta}\right)_{V,n} = \left(\frac{\partial}{\partial \beta} \sum_{i=1}^{\infty} e^{-\beta E_i}\right)_{V,n} = -\sum_{i=1}^{\infty} e^{-\beta E_i} \times E_i \tag{1.19}$$

Comparing this with Eq. (1.18) leads to:

$$U(T) = -\frac{1}{Z}\left(\frac{\partial Z}{\partial \beta}\right)_{V,n} = -\left(\frac{\ln(Z)}{\partial \beta}\right)_{V,n} \tag{1.20}$$

This means that the internal energy can be obtained from Z by applying the above mathematical operation on it (vrt. operators in quantum mechanics). Remember that it will turn out that $\beta = \beta(T)$, so the differentiations in Eq. (1.20) will actually be with respect to temperature T.

1.4 Evaluation of pressure

Since P is not fixed in canonical ensemble, we have to derive an expression for it in terms of the ensemble state variables (T, V, n). In a smilar way to internal energy, pressure is obtained as ensemble average:

$$P = \langle P_i \rangle = \sum_{i=1}^{\infty} p_i P_i \tag{1.21}$$

where P_i is the pressure of the ith member of the ensemble. Note that the value of P_i varies from one ensemble member to another.

Based on the classical thermodynamics notes, the change in internal energy for an adiabatic process can be written in two ways:

$$dU = dw_{rev} = -PdV \text{ and } dU = \left(\frac{\partial U}{\partial V}\right) dV \tag{1.22}$$

which can be combined to give:

$$P = -\left(\frac{\partial U}{\partial V}\right) \tag{1.23}$$

This should apply also to each ensemble member (where $U \mapsto E_i$) and therefore Eq. (1.21) can be written as (see also Eq. (1.17)):

$$P = -\frac{1}{Z} \sum_{i=1}^{\infty} e^{-\beta E_i} \left(\frac{\partial E_i}{\partial V}\right)_n \tag{1.24}$$

To see how the above expression is related to the partition function, we differentiate Z with respect to volume V:

$$\left(\frac{\partial Z}{\partial V}\right)_{T,n} = \sum_{i=1}^{\infty}\left(\frac{\partial e^{-\beta E_i}}{\partial V}\right)_{T,n} \tag{1.25}$$

$$= \sum_{i=1}^{\infty} \frac{\partial\left(e^{-\beta E_i}\right)}{\partial E_i} \times \frac{\partial E_i}{\partial V} = -\sum_{i=1}^{\infty} \beta e^{-\beta E_i}\left(\frac{\partial E_i}{\partial V}\right)_{T,n}$$

So, we can combined Eqs. (1.24) and (1.25) to yield:

$$P = \frac{1}{\beta Z}\left(\frac{\partial Z}{\partial V}\right)_{T,n} = \frac{1}{\beta}\left(\frac{\partial \ln(Z)}{\partial V}\right)_{T,n} \tag{1.26}$$

This follows the same pattern as we saw for internal energy U: a mathematical operation (that depends on V, T, n) extracts pressure from the partition function.

1.5 Determination of β

We begin by differentiating Eq. (1.20) with respect to V:

$$\begin{aligned} \left(\frac{\partial U}{\partial V}\right)_T &= -\left[\frac{\partial}{\partial V}\left(\frac{\partial \ln(Z)}{\partial \beta}\right)_{V,n}\right]_T \qquad (1.27) \\ &= -\left[\frac{\partial}{\partial \beta}\left(\frac{\partial \ln(\beta)}{\partial V}\right)_T\right]_V \overbrace{=}^{(1.26)} -\left[\frac{\partial}{\partial \beta}(\beta P)\right]_V \\ &= -P - \beta\left(\frac{\partial P}{\partial \beta}\right)_V \end{aligned}$$

Next we use the following result from classical thermodynamics:

$$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V - P \qquad (1.28)$$

The first term on the right can be written in a different form as:

$$\frac{\partial P}{\partial T} = \frac{\partial P}{\partial(1/T)} \times \underbrace{\frac{\partial(1/T)}{\partial T}}_{=-1/T^2} = -\frac{1}{T^2}\frac{\partial P}{\partial(1/T)} \qquad (1.29)$$

Inserting this into Eq. (1.28) gives:

$$\left(\frac{\partial U}{\partial V}\right)_T = T \times \left(-\frac{1}{T^2}\right) \times \left(\frac{\partial P}{\partial (1/T)}\right)_V - P = -\frac{1}{T}\left(\frac{\partial P}{\partial (1/T)}\right)_V - P \qquad (1.30)$$

This can be compared with Eq. (1.27) and we see that the last terms on the right in these equationsmust be equal:

$$\beta\left(\frac{\partial P}{\partial \beta}\right)_V = \frac{1}{T}\left(\frac{\partial P}{\partial (1/T)}\right)_V \qquad (1.31)$$

This equation is statisfied if $\beta \propto 1/T$. The proportionality constant is called the Boltzmann constant ($k = 1.38066 \times 10^{-23}$ J/K):

$$\beta = \frac{1}{kT} \qquad (1.32)$$

This gives the complete form for the partition function Z and the ensemble probability p_i:

$$Z = \sum_{j=1}^{\infty} e^{-E_j/(kT)} \qquad (1.33)$$

$$p_i = \frac{1}{Z} e^{-E_i/(kT)}$$

We can now substitute the expression $\beta = \frac{1}{kT}$ in Eqs. (1.20) and (1.26):

$$U = -\left(\frac{\partial \ln(Z)}{\partial \beta}\right)_{V,n} = -\left(\frac{\partial \ln(Z)}{\partial T}\right) \times \underbrace{\left(\frac{dT}{d\beta}\right)}_{=-\frac{1}{k\beta^2}} = kT^2 \left(\frac{\partial \ln(Z)}{\partial T}\right)_{V,n} \tag{1.34}$$

$$P = \frac{1}{\beta}\left(\frac{\partial \ln(Z)}{\partial V}\right)_{T,n} = kT\left(\frac{\partial \ln(Z)}{\partial V}\right)_{T,n} \tag{1.35}$$

1.6 Evaluation of entropy

When only PV-work takes place, the 1st and 2nd laws of thermodynamics can be combined into (see classical thermodynamics notes):

$$dU = TdS - PdV \text{ (natural variables } S, V) \tag{1.36}$$

Solving for dS:

$$dS = \frac{dU}{T} + \frac{PdV}{T} \tag{1.37}$$

Next we apply the following equation to Eq. (1.37):

$$d\left(\frac{U}{T}\right) = -\frac{U}{T^2}dT + \frac{dU}{T} \Rightarrow \frac{dU}{T} = d\left(\frac{U}{T}\right) + \frac{U}{T^2}dT \tag{1.38}$$

Inserting this to Eq. (1.37) gives:

$$dS = d\left(\frac{U}{T}\right) + \frac{U}{T^2}dT + \frac{PdV}{T} \tag{1.39}$$

The expressions for U and P are known (see Eqs. (1.34) and (1.35)) and these can be inserted above:

$$dS = d\left(\frac{U}{T}\right) + k\left(\frac{\partial \ln(Z)}{\partial T}\right)_{V,n} dT + k\left(\frac{\partial \ln(Z)}{\partial V}\right)_{T,n} dV \tag{1.40}$$

The total differential for $\ln(Z)$ can be written as:

$$d\ln(Z) = \left(\frac{\partial \ln(Z)}{\partial T}\right)_{V,n} dT + \left(\frac{\partial \ln(Z)}{\partial V}\right)_{T,n} dV \tag{1.41}$$

This corresponds to the last two terms in Eq. (1.40) and hence we can rewrite Eq. (1.40) as:

$$dS = d\left(\frac{U}{T}\right) + kd(\ln(Z)) = d\left(\frac{U}{T} + k\ln(Z)\right) \tag{1.42}$$

Both sides can be intergrated:

$$\int_{S(0)}^{S(T)} dS = \int_{g(0)}^{g(T)} d\underbrace{\left(\frac{U}{T} + k\ln\left(Z\right)\right)}_{\equiv g} \tag{1.43}$$

which leads to (recall 3rd law of thermodynamics; $S(0) = 0$):

$$S(T) = \frac{U(T)}{T} + k\ln\left(Z(T)\right) - \lim_{T\to 0}\left[\frac{U(T)}{T} + k\ln\left(Z(T)\right)\right] \tag{1.44}$$

For most systems the limit is zero (* see below) and Eq. (1.44) simplifies to:

$$S(T) = \frac{U(T)}{T} + k\ln\left(Z(T)\right) = kT\left(\frac{\partial \ln(Z)}{\partial T}\right)_{V,n} + k\ln(Z) \tag{1.45}$$

This expression gives the sought prescription for extracting entropy from the partition function.

(*) Confined quantum mechanical systems have zero-point energy and therefore $U(T) \to E_1$ (the lowest energy configutation with only zero-point energy contributing) when $T \to 0$. In this limit, the first term in Eq. (1.44) becomes simply E_1/T. For the second term, $k\ln(Z(T))$, only the lowest state (state 1) contributes to Z and therefore (see Eq. (1.33)) $k\ln(Z(T)) = -E_1/T$. Note that classical systems do not have zero-point energy and $E_1 = 0$.

Note that the above reasoning can also be used to show that Eq. (1.44) is compatible with the 3rd law of thermodynamics (i.e., $S(T) \to 0$ when $T \to 0$). This consideration does not account for the possible degeneracy of the lowest state (residual entropy).

1.7 Other thermodynamic functions

Recall from classical thermodynamics (Legendre transformations) that the following thermodynamic functions were defined:

$$\begin{aligned} H &= U + PV \text{ (enthalpy)} \\ A &= U - TS \text{ (Helmoltz energy)} \\ G &= H - TS = U + PV - TS \text{ (Gibbs energy)} \end{aligned} \tag{1.46}$$

Since V, T, and n are constant in canonical ensemble and expressions for U, P, and S were derived previously, H, A, and G can be obtained.

Below is a summary of the results based on Eq. (1.46):

$$H = kT^2\left(\frac{\partial \ln(Z)}{\partial T}\right)_{V,n} + VkT\left(\frac{\partial \ln(Z)}{\partial V}\right)_{T,n} \tag{1.47}$$

$$A = -kT\ln(Z) \tag{1.48}$$

$$G = VkT\left(\frac{\partial \ln(Z)}{\partial V}\right)_{T,n} - kT\ln(Z) \tag{1.49}$$

1.8 The Boltzmann postulate for entropy

The Boltzmann postulate for entropy states (recall from classical thermodynamics) that:

$$S = k \ln{(\Omega)} \tag{1.50}$$

where Ω is the number of microscopic ways to arrange the system. The origin of this result can be seen starting from Eq. (1.45):

$$S = \frac{U}{T} + k \ln(Z)$$

Inserting the definition of U (Eq. 1.18):

$$U = \frac{1}{Z} \sum_{i=1}^{\infty} e^{-E_i/(kT)} \times E_i = -\frac{kT}{Z} \sum_{i=1}^{\infty} \ln\left(e^{-E_i/(kT)}\right) \times e^{-E_i/(kT)}$$

Inserting this into the expression for S gives:

$$S = -\frac{k}{Z} \sum_{i=1}^{\infty} \ln\left(e^{-E_i/(kT)}\right) \times e^{-E_i/(kT)} + k \ln(Z) \tag{1.51}$$

Since $\sum_{i=1}^{\infty} e^{-E_i/(kT)} Z = 1$, we can modify the last term:

$$S = -\frac{k}{Z} \sum_{i=1}^{\infty} \ln\left(e^{-E_i/(kT)}\right) \times e^{-E_i/(kT)} + \frac{k}{Z} \sum_{i=1}^{\infty} e^{-E_i/(kT)} \ln(Z) \tag{1.52}$$

Combining the terms in Eq. (1.52) gives:

$$S = -k \sum_{i=1}^{\infty} \underbrace{\frac{e^{-E_i/(kT)}}{Z}}_{=p_i} \times \left(\ln \left(e^{E_i/(kT)} \right) - \ln(Z) \right) \tag{1.53}$$

$$= -k \sum_{i=1}^{\infty} p_i \ln \underbrace{\left(\frac{e^{E_i/(kT)}}{Z} \right)}_{=p_i} = -k \sum_{i=1}^{\infty} p_i \ln \left(p_i \right)$$

This called the Gibbs equation for entropy. If all states have the same probability of occurring, $p_i \equiv 1/\Omega$ (Ω is the number of possible configurations), then Eq. (1.53) can be written as:

$$S = -k \sum_{i=1}^{\Omega} \frac{1}{\Omega} \ln \left(\frac{1}{\Omega} \right) = k \ln \left(\Omega \right) \tag{1.54}$$

where the limit $\Omega \to \infty$ should be taken.

Chapter 2: Thermodynamics of non-interacting monatomic gas

“Compute the partition function for the system and let the machinery do the rest!”

2.1 The atomic partition function

We will apply the concepts developed in the previous chapter to monatomic (only translation) ideal gas (no interaction between atoms). Assume a classical system where the particles are distinguishable (i.e., no states exlcuded).

The energy of an ensemble member identified by an n-dimensional vector $(k, l, ..., m)$, which plays the role of summation index i in Eq. (2.1), is:

$$E_{(k,l,...m)} = \epsilon_{k,1} + \epsilon_{l,2} + ... + \epsilon_{m,n} \tag{2.1}$$

where $\epsilon_{k,j}$ is the energy of atom j in state k. Because the particles are identical and do not interact, they occupy the same atomic states. The (canonical) partition function can now be written as ($\beta = \frac{1}{kT}$):

$$\begin{aligned} Z &= \sum_{\substack{k=1,l=1\\ \dots,m=1}}^{\infty} e^{-\beta E_{(k,l,\dots,m)}} \qquad (2.2) \\ &= \underbrace{\sum_{k=1}^{\infty}\sum_{l=1}^{\infty}\cdots\sum_{m=1}^{\infty}}_{n\text{ summations}} e^{-\beta\left(\epsilon_{k,1}+\epsilon_{l,2}+\dots+\epsilon_{m,n}\right)} \end{aligned}$$

Eq. (2.2) can be separated into a product:

$$Z = \underbrace{\sum_{k=1}^{\infty} e^{-\beta\epsilon_{k,1}}}_{\text{Atom \#1}} \times \underbrace{\sum_{l=1}^{\infty} e^{-\beta\epsilon_{l,2}}}_{\text{Atom \#2}} \times \cdots \times \underbrace{\sum_{m=1}^{\infty} e^{-\beta\epsilon_{m,n}}}_{\text{Atom \#}n} \tag{2.3}$$

The atoms occupy identical energy levels ($\epsilon_{i,1} = \epsilon_{i,2} = ... = \epsilon_{i,n} \equiv \epsilon_i$) without restrictions and hence all the terms above are identical:

$$Z = \left(\sum_{i=1}^{\infty} e^{-\beta\epsilon_i}\right)^n \tag{2.4}$$

The individual components in Eq. (2.3) are called *atomic partition functions*:

$$z_j \equiv \sum_{i=1}^{\infty} e^{-\beta\epsilon_{i,j}} \tag{2.5}$$

With this notation, Eq. (2.3) becomes:

$$Z = z_1 \times z_2 \times ... \times z_n \tag{2.6}$$

and Eq. (2.4) is then:

$$Z = z^n \tag{2.7}$$

where we imposed $z = z_1 = z_2 = ... = z_n$.

If the atoms are distinguishable we can tell, for example, the difference between atom 1 in state 1 and atom 2 in state 2 VS. atom 1 in state 2 and atom 2 in state 1. In this case Eq. (2.7) is correct. However, according to quantum mechanics identical particles should be *indistinguishable*. Therefore the above construction leads to inclusion of states that do not exist. For example, the two configurations mentioned above correspond to the same state and should not be included twice. The number of distinct ways to distribute n atoms over a large number of states is approximately given by factorial, $n!$, and therefore we should normalize Eq. (2.4):

$$Z = \frac{z^n}{n!} \tag{2.8}$$

However, this approximation fails at low temperatures (exclusion of states) and we will return to this point later.

2.2 Translational partition function

We model the atoms as “particle in a 3-D box” (quantum mechanics) and consider them as indistinguishable particles. The box could correspond to the container where the atoms are constrained in. The *translational partition function* can then be written as (see Eq. (2.8)):

$$Z_{tr} = \frac{(z_{tr})^n}{n!} = \frac{1}{n!}\left(\sum_{n_x=1}^{\infty}\sum_{n_y=1}^{\infty}\sum_{n_z=1}^{\infty} e^{-\beta E(n_x,n_y,n_z)}\right)^n \tag{2.9}$$

where the energy of the system is determined by the quantum numbers n_x, n_y, n_z:

$$E\left(n_x,n_y,n_z\right) = \frac{h^2}{8m}\left(\frac{n_x^2}{a^2}+\frac{n_y^2}{b^2}+\frac{n_z^2}{c^2}\right) \tag{2.10}$$

where a, b, and c correspond to the box side lengths. Since the energy levels are very close to each other, we can replace the summations in Eq. (2.10) by integrals (i.e., discrete vs. continuous):

$$\sum_{n_x}^{\infty} e^{-\left(\beta h^2/(8m)\right)n_x^2/a^2} \approx \int_0^{\infty} e^{-\left(\beta h^2/(8m)\right)n_x^2/a^2}\,dn_x = \frac{1}{2}\left(\frac{8m\pi}{\beta h^2}\right)^{1/2} a \tag{2.11}$$

where the last step involves integration of $\int_0^\infty e^{-ax^2}$ (from mathematics handbook).

Therefore the atomic partition function z_{tr} is:

$$z_{tr} = \left(2\pi mkT/\hbar^2\right)^{3/2} V \text{ where } V = abc \text{ (volume)} \tag{2.12}$$

Taking natural logarithm of Eq. (2.12):

$$\ln(z_{tr}) = \frac{3}{2}\ln\left(2\pi mk/h^2\right) + \frac{3}{2}\ln(T) + \ln(V) \tag{2.13}$$

The (total) translational partition function is then given by (see Eq. (2.8)):

$$\ln\left(Z_{tr}\right) = \ln\left(\frac{z_{tr}^n}{n!}\right) = n\ln\left(z_{tr}\right) - \ln\left(n!\right) \tag{2.14}$$

2.3 Calculation of internal energy

To calculate the internal energy of monatomic ideal gas, we start with Eq. (1.34):

$$U = kT^2 \left(\frac{\partial \ln(Z_{tr})}{\partial T}\right)_{V,n}$$

Based on Eq. (2.14), we can compute the required derivative above as follows:

$$\left(\frac{\partial \ln\left(Z_{tr}\right)}{\partial T}\right)_{V,n} = \frac{\partial}{\partial T}\left(n \ln\left(z_{tr}\right) - \underbrace{\ln\left(n!\right)}_{\to 0}\right) \tag{2.15}$$

$$= n\frac{\partial}{\partial T}\left(\frac{3}{2}\underbrace{\ln\left(2\pi mk/h^2\right)}_{\to 0} + \frac{3}{2}\ln(T) + \underbrace{\ln(V)}_{\to 0}\right)_{V,n} = \frac{3}{2}n/T$$

Inserting this into the expression for U gives:

$$U = kT^2 \times \frac{3}{2}\frac{n}{T} = \frac{3}{2}nkT \tag{2.16}$$

This can be written in terms of per mole quantities as (n in moles):

$$U = \frac{3}{2}nRT \tag{2.17}$$

where R is related to k by Avogadro's number: $R = k \times N_a = 8.31451$ J / (mol K).

2.4 Calculation of entropy

To calculate entropy, we start with Eq. (1.45):

$$S = \frac{U}{T} + k \ln(Z_{tr})$$

and use Eq. (2.14) for Z_{tr}:

$$\begin{aligned} \ln\left(Z_{tr}\right) &= n \ln\left(z_{tr}\right) - \ln\left(n!\right) \\ &= n\left[\frac{3}{2}\ln\left(2\pi mk/h^2\right) + \frac{3}{2}\ln(T) + \ln(V)\right] - \ln\left(n!\right) \end{aligned}$$

This gives the following expression for entropy S:

$$\begin{aligned} S &= \frac{3}{2}nk + \frac{3}{2}nk\ln\left(2\pi mk/h^2\right) + \frac{3}{2}nk\ln\left(T\right) + nk\ln\left(V\right) - k\ln\left(n!\right) \quad (2.18) \\ &= nk\left(\frac{3}{2} + \frac{3}{2}\ln\left(\frac{2\pi mkT}{h^2}\right) + \ln(V) - \frac{1}{n}\ln(n!)\right) \\ &= nk\left(\frac{3}{2} + \ln\left(\left(\frac{2\pi mkT}{h^2}\right)^{3/2} V\right) - \frac{1}{n}\ln(n!)\right) \end{aligned}$$

The last term on the right can be rewritten using Stirling's approximation (n sufficiently large):

$$\ln(n!) \approx n\ln(n) - n \tag{2.19}$$

Thus the last term becomes:

$$-\frac{1}{n}\ln(n!) \approx -\frac{1}{n}\left(n\ln(n) - n\right) = -\ln(n) + 1 \tag{2.20}$$

Rewriting Eq. (2.18) now gives the final result (for monatomic ideal gas):

$$\begin{aligned} S &= nk\left(\frac{3}{2} + \ln\left(\left(\frac{2\pi mkT}{h^2}\right)^{3/2}\frac{V}{n}\right) + 1\right) \qquad (2.21) \\ &= nk\left(\frac{5}{2} + \ln\left(\left(\frac{2\pi mkT}{h^2}\right)^{3/2}\frac{V}{n}\right)\right) \end{aligned}$$

This is a special case of so-called Sackur-Tetrode equation:

$$S = nk\left[\frac{5}{2} + \ln\left(\left(\frac{4\pi m}{3h^2}\frac{U}{n}\right)^{3/2}\frac{V}{n}\right)\right] \tag{2.22}$$

which is a good approximation when $\frac{V}{n}\left(\frac{2\pi mkT}{h^2}\right)^{3/2} >> 1$.

2.5 Pressure of monatomic ideal gas

First recall the ideal gas law from classical thermodynamics: $PV = nkT$ (or $PV = nRT$ in terms of moles). In the following, we will see how this result originates from statistical thermodynamics.

Pressure is given by Eq. (1.26):

$$P = kT\left(\frac{\partial \ln\left(Z_{tr}\right)}{\partial V}\right)_{T,n}$$

The partial derivative above can be calculated from the translational partition function (Eqs. (2.13) and (2.14)):

$$\ln\left(Z_{tr}\right) = N\ln\left(z_{tr}\right) - \ln\left(N!\right)$$

$$\ln\left(z_{tr}\right) = \frac{3}{2}\ln\left(2\pi mk/h^2\right) + \frac{3}{2}\ln(T) + \ln(V)$$

So we get simply:

$$\left(\frac{\partial \ln\left(Z_{tr}\right)}{\partial V}\right)_{T,n} = \frac{n}{V} \tag{2.23}$$

and the pressure is then:

$$P = kT\frac{n}{V} = nkT/V \text{ or } PV = nkT \tag{2.24}$$

2.6 Enthalpy and heat capacity of monatomic ideal gases

Based on Eqs. (1.46), (2.17), and (2.25), we can write the enthalpy as:

$$H = U + PV = \frac{3}{2}nkT + \frac{nkT}{V} \times V = \frac{5}{2}nkT \left(= \frac{5}{2}nRT \right) \tag{2.25}$$

Constant volume and pressure heat capacities can be written accordingly as:

$$C_V = \left(\frac{\partial U}{\partial T} \right)_V = \frac{\partial}{\partial T} \left(\frac{3}{2}nkT \right) = \frac{3}{2}nk \left(= \frac{3}{2}nR \right) \tag{2.26}$$

$$C_P = \left(\frac{\partial H}{\partial T} \right)_P = \frac{\partial}{\partial T} \left(\frac{5}{2}nkT \right) = \frac{5}{2}nk \left(= \frac{5}{2}nR \right) \tag{2.27}$$

where the expressions given in parentheses are written in terms of moles.

2.7 Test case: Ideal gases

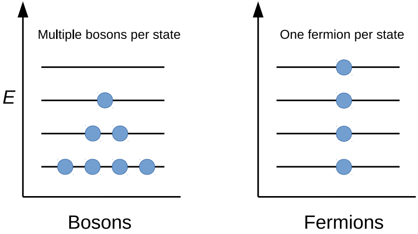
Rare gases (or noble gases) at 1 bar and 298 K provide a good test for the previously developed results. A comparison between the experimental values (*exp*) of absolute molar entropies (S°; J K^{-1} mol^{-1}) and constant pressure heat capacities (C_P; J K^{-1} mol^{-1}) against statistical thermodynamics (i.e., Eqs. (2.23) and (2.27); *theo*) is shown below. Despite the weak attractive van der Waals and short-range repulsive interactions between the atoms, the pressure is sufficiently low and temperature high such that these interactions do not contribute to the results (i.e., ideal gas behavior).

Gas	S°_{exp}	S°_{theo}	$C_{P,exp}$	$C_{P,theo}$
He	126.15	126.14	20.786	20.786
Ne	146.33	146.32	20.786	20.786
Ar	154.84	154.84	20.786	20.786
Kr	164.08	164.08	20.786	20.786
Xe	169.68	169.68	20.768	20.768

Note that Eq. (2.21) explains the dependence of entropy on the atomic mass, which often stated in introductory chemistry textbooks.

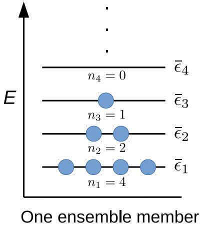
2.8 Monatomic systems at low temperatures

According to quantum mechanics, indistinguishable particles can be classified as bosons (integer spin; 0, 1, 2, ...) or fermions (half-integer spin; 1/2, 3/2, ...). The main difference between the two is that only one fermion can occupy a given (discrete) state whereas multiple bosons can occupy the same state. The former is called the *Pauli exclusion principle* (fermions only).



Examples. Bosons: ^{4}He nucleus (spin 0), ^{14}N nucleus (spin 1), photon (spin 1; $m_s = \pm 1$, no $m_s = 0$!). Fermions: ^{3}He nucleus (spin 1/2), electron (spin 1/2).

Average occupation of discrete energy levels:



The total energy of ensemble member i is given by:

$$E_i = n_{i,1}\bar{\epsilon}_1 + n_{i,2}\bar{\epsilon}_2 + ... = \sum_{j=1}^{\infty} n_{i,j}\bar{\epsilon}_j \tag{2.28}$$

with a fixed number of particles N:

$$\sum_{j=1}^{\infty} n_{i,j} = N \tag{2.29}$$

The partition function is then (similar to Eq. (2.2)):

$$Z = \sum_{i=1}^{\infty} e^{-\beta E_i} = \sum_{i=1}^{\infty} \exp\left(-\beta\left(n_{i,1}\bar{\epsilon}_1 + n_{i,2}\bar{\epsilon}_2 + ...\right)\right) \tag{2.30}$$

where i index corresponds to the ensemble member number and j to the energy level.

The average occupation number of state j is defined as:

$$\langle n_j \rangle = \sum_{i=1}^{\infty} p_i n_{i,j} \tag{2.31}$$

where p_i is the probability for ensemble member i to occur:

$$p_i = \frac{1}{Z} \exp\left(-\beta\left(n_{i,1}\bar{\epsilon}_1 + n_{i,2}\bar{\epsilon}_2 + \ldots\right)\right) \tag{2.32}$$

We can now derive an expression for the occupation number in terms of the partition function:

$$\begin{aligned}
\langle n_j \rangle &= \sum_{i=1}^{\infty} p_i n_{i,j} = \sum_{i=1}^{\infty} \frac{\exp\left(-\beta \sum_{k=1}^{\infty} n_{i,k}\bar{\epsilon}_k\right)}{Z} n_{i,j} \qquad (2.33) \\
&= \frac{1}{Z}\left(-\frac{1}{\beta}\frac{\partial}{\partial \bar{\epsilon}_j}\right) \underbrace{\sum_{i=1}^{\infty} \exp\left(-\beta \sum_{k=1}^{\infty} n_{i,j}\bar{\epsilon}_k\right)}_{=Z} = -\frac{1}{\beta Z}\frac{\partial Z}{\partial \bar{\epsilon}_j} \\
&= -\frac{1}{\beta}\frac{\partial \ln(Z)}{\partial \bar{\epsilon}_j} = -kT\frac{\partial \ln(Z)}{\partial \bar{\epsilon}_j}
\end{aligned}$$

Classical Maxwell-Boltzmann distribution:

Consider distinguishable (classical) ideal gas. The partition function and ensemble energy can be written as:

$$Z = \left(\sum_{i=1}^{\infty} e^{-\beta\bar{\epsilon}_i}\right)^n \Rightarrow \ln(Z) = n\ln\left(\sum_{i=1}^{\infty} e^{-\beta\bar{\epsilon}_i}\right)$$

$$E_i = \sum_{j=1}^{\infty} n_{i,j}\bar{\epsilon}_j$$

Inserting these into Eq. (2.33) gives:

$$\langle n_j\rangle = -\frac{1}{\beta}\frac{\partial}{\partial\bar{\epsilon}_j}\left(n\ln\left(\sum_{i=1}^{\infty} e^{-\beta\bar{\epsilon}_i}\right)\right) \tag{2.34}$$

$$= -\frac{n}{\beta}\frac{1}{\sum_{i=1}^{\infty} e^{-\beta\bar{\epsilon}_i}} \times \frac{\partial}{\partial\bar{\epsilon}_j}\sum_{i=1}^{\infty} e^{-\beta\bar{\epsilon}_i} = n\frac{e^{-\beta\bar{\epsilon}_j}}{\sum_{i=1}^{\infty} e^{-\beta\bar{\epsilon}_i}}$$

Therefore the statistical weights, w_j, in the *Maxwell-Boltzmann distribution* are given by:

$$w_j = \frac{\langle n_j\rangle}{n} = \frac{e^{-\beta\bar{\epsilon}_j}}{\sum_{i=1}^{\infty} e^{-\beta\bar{\epsilon}_i}} \text{ where } \beta = \frac{1}{kT} \tag{2.35}$$

Quantum Bose-Einsten distribution (bosons):

Bosons can occupy the single-particle states without any restrictions and we should treat them as indistinguishable. The partition function is now given by (sampling over all possible configurations such that $n_1 + n_2 + ... = n$):

$$
\begin{aligned}
Z = \sum_{i=1}^{\infty} e^{-\beta E_i} = \sum_{\substack{n_1=0,1,2,\ldots \\ n_2=0,1,2,\ldots \\ \ldots}} e^{-\beta(n_1\bar{\epsilon}_1 + n_2\bar{\epsilon}_2 + \ldots)} = \sum_{\substack{n_1=0,1,2,\ldots \\ n_2=0,1,2,\ldots \\ \ldots}} e^{-\beta n_1 \bar{\epsilon}_1} \\
\times e^{-\beta n_2 \bar{\epsilon}_2} \times ... = \left(\sum_{n_1=0} e^{-\beta n_1 \bar{\epsilon}_1} \right) \times \left(\sum_{n_2=0} e^{-\beta n_2 \bar{\epsilon}_2} \right) \times ...
\end{aligned}
\tag{2.36}
$$

Extending the limits in the last summations above to infinity (large number of particles), we can turn the individual sums into geometric series. For example, for state 1:

$$\sum_{n_1=0}^{\infty} e^{-\beta n_1 \bar{\epsilon}_1} = 1 + e^{-\beta \bar{\epsilon}_1} + e^{-2\beta \bar{\epsilon}_1} + ... = \frac{1}{1 - e^{-\beta \bar{\epsilon}_1}} \tag{2.37}$$

Thus we can write the partition function as follows:

$$Z = \left(\frac{1}{1 - e^{-\beta \bar{\epsilon}_1}} \right) \times \left(\frac{1}{1 - e^{-\beta \bar{\epsilon}_2}} \right) \times ... \tag{2.38}$$

Taking natural log of both sides above gives:

$$\ln(Z) = -\sum_{i=1}^{\infty} \ln\left(1 - e^{-\beta\bar{\epsilon}_i}\right) \tag{2.39}$$

Eq. (2.33) can be used to compute the average occupation number:

$$\langle n_j \rangle = -\frac{1}{\beta}\frac{\partial \ln(Z)}{\partial \bar{\epsilon}_j} = \frac{1}{\beta}\frac{\partial}{\partial \bar{\epsilon}_j}\left(\sum_{i=1}^{\infty} \ln\left(1 - e^{-\beta\bar{\epsilon}_i}\right)\right) \tag{2.40}$$

$$= \frac{1}{\beta}\frac{\partial}{\partial \bar{\epsilon}_j}\left(\ln\left(1 - e^{-\beta\bar{\epsilon}_j}\right)\right) = \frac{e^{-\beta\bar{\epsilon}_j}}{1 - e^{-\beta\bar{\epsilon}_j}} = \frac{1}{e^{\beta\bar{\epsilon}_j} - 1}$$

Based on this result, the statistical weight of state j is:

$$w_j = \frac{\langle n_j \rangle}{n} = \frac{1}{n\left(e^{\beta\bar{\epsilon}_j} - 1\right)} \tag{2.41}$$

In order to conserve the total number of particles (n), an additional constant (chemical potential; μ) should be included above:

$$w_j = \frac{\langle n_j \rangle}{n} = \frac{1}{n\left(e^{\beta\left(\bar{\epsilon}_j - \mu\right)} - 1\right)} \tag{2.42}$$

Quantum Fermi-Diract distribution (fermions):

Since only one fermion can occupy a given state, some configurations must be excluded from the above calculation (Pauli exclusion principle). It can be shown that in this case Eq. (2.42) becomes:

$$w_j = \frac{\langle n_j \rangle}{n} = \frac{1}{n\left(e^{\beta(\bar{\epsilon}_j - \mu)} + 1\right)} \tag{2.43}$$

Note that for degenerate states, both Eqs. (2.41) and (2.42) should include the degeneracy factor (i.e., they should be multiplied by it).