Statistical Mechanics of Diatomic Gases

1- For monatomic gas, whose molecules have three degrees of freedom of translatory motion, the internal energy and the specific heat of one mole of gas are \( u = \frac{3}{2} RT \), and \( c_v = \left( \frac{\partial u}{\partial T} \right)_v = \frac{3}{2} R \), respectively.

The energy does not depend upon the volume.

2- A molecule is a stable compound of two like or different atoms.

3- The nature of forces that leads to the formation of a molecule from isolated atoms is treated in quantum mechanics.

4- The energy of the molecule is made up of:
   i. The translation kinetic energy of its center of mass \( E_{\text{trans}} \).
   ii. Energy of excitation of the atomic electrons in the molecule \( E_e \).
   iii. Energy of vibration of the nuclei along the axis joining them, \( E_{\text{vib}} \), and
   iv. The rotational kinetic energy due to the rotational motion of the atoms about the center of mass of the molecule, \( E_{\text{rot}} \). Thus

\[ E = E_{\text{trans}} + E_e + E_{\text{rot}} + E_{\text{vib}} \]

The translational motion of a diatomic molecule is not quantized. All the other kinds of internal motion of the molecule are quantized, i.e. \( E_e, E_{\text{rot}}, \) and \( E_{\text{vib}} \) assume a discrete series of values.

Approximations:
I- Assume that the three kind of internal motion of molecule are independent of one another.
II- The influence of vibrational motion on rotation can be neglected. i.e. the moments of inertial of molecules stay constant.
III- \( \Delta E_e \approx 1 \text{eV} \approx 10^4 \text{K} \) i.e. very high temperature is required to produce a substantial number of molecules in excited electronic states. This is why we are neglecting the contribution of the electronic states.

IV- Because of \( \Delta E_{\text{vib}} \approx 10^{-3} \text{eV} \) to \( 10^{-1} \text{eV} \), \( \Delta E_{\text{rot}} \approx 10^{-4} \) then it is easy to find a few vibrational and rotation states at room temperature.

Vibrational modes:

For an oscillator with mass \( m \) and angular frequency \( \omega = 2\pi f \), the Hamiltonian in three dimensions is:

\[ H(p,q) = \frac{p^2}{2m} + \frac{1}{2} \frac{m\omega^2 q^2}{2} \]

and the vibrational energy level is given by:

\[ \epsilon_j = (j + \frac{1}{2}) \hbar \omega, \quad j = 0, 1, 2, \ldots \]

Note That:
- The energies are equally spaced, i.e. \( \Delta \epsilon_j = \hbar \omega \),
- The ground state has “zero point” energy equal to \( \hbar \omega / 2 \),
- The states are non-degenerate, i.e. \( g_j = 1 \) for all \( j \).
The partition function: (use the geometric series summation
\[ \sum_{v=0}^{\infty} e^{-\beta e_v} = \frac{1}{1 - e^{-a}} \])

\[ z_{vib} = \sum_{v} e^{-\beta e_v} = e^{-a} \sum_{v} e^{-\beta v(2a)} = \frac{e^{-a}}{1 - e^{-2a}} = \frac{1}{e^{a} - e^{-a}} = (2\sinh a)^{-1}, \quad a = \frac{\theta_{vib}}{2T}, \quad \theta_{vib} = \frac{\hbar \omega}{k_B} \]

**Note that:** the value of \( \theta_{vib} \) (has a units of temperature K) separates between the quantum and classical regions.

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**Example:** If you know that \( \hbar \omega = 0.29 \) eV for \( \text{N}_2 \), then \[ \theta_{vib} = \frac{\hbar \omega}{k_B} = \frac{0.29 \times 1.6 \times 10^{-10}}{1.38 \times 10^{-23}} \frac{\text{J}}{\text{K}} = 3362 \text{ K}. \]

So, any temperature less than or equal 3362 K will be in quantum region, and any temperature greater than 3362 K will be in classical region.

H.W. Calculate \( \theta_{vib} \) for \( \text{H}_2, \text{O}_2, \) and \( \text{Cl}_2 \).

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**We shall also be concerned with the occupation numbers, or with** \( P_j = N_j / N \), the fraction of the total number of particles with energy \( \epsilon_j \). The Boltzmann distribution for \( g_i = 1 \) is

\[ P_j = \frac{N_j}{N} = \frac{e^{-\beta \epsilon_j} - e^{-\beta \epsilon_j}}{z_{vib}} = e^{-\beta \epsilon_j} e^a (1 - e^{-2a}) = (1 - e^{-2a}) e^{-\beta \epsilon_j + a} \]

The exponent of the term outside the parentheses can be written

\[ -\beta \epsilon_j + a = -\frac{1}{k_B T} (j + \frac{1}{2}) \frac{h \nu}{k_B T} + \frac{h \nu}{2k_B T} = -j \frac{h \nu}{k_B T} = -ja = -j \frac{\theta_{vib}}{T} \]

Thus

\[ P_j = \frac{N_j}{N} = (1 - e^{-\frac{\theta_{vib}}{T}}) e^{-j \frac{\theta_{vib}}{T}} \]

A sketch of the last equation for two temperatures shows that the lower the temperature, the more rapidly the occupation numbers decrease with \( j \) (Figure 15.1). At higher temperatures, more particles populate the higher energy levels.

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**The single particle partition function leads to a heat capacity of**

\[ C_{vib} = \frac{\partial U_{vib}}{\partial T} \bigg|_{V,N} = Nk_B \left( \frac{\theta_{vib}}{T} \right)^2 \frac{e^{\frac{\theta_{vib}}{T}}}{e^{\frac{\theta_{vib}}{T}} - 1} \]

This heat capacity decays exponentially as \( T \ll \theta_{vib} \) and tends to zero as \( T \to 0 \), and tends to \( R \) per mole as \( T \gg \theta_{vib} \).
Quantity & Formula & $T \to 0$ & $T \to \infty$
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Partition function & $Z_{vib} = z_{vib}^N = (2 \sinh a)^{-N}$ & 0? & $(\frac{k_B T}{\hbar \omega})^N$
Helmholtz free energy & $F = -k_B T \ln Z_{vib} = N k_B T \ln(2 \sinh a)$ & 0? & $F = N k_B T \ln(\beta \hbar \omega)$
Entropy & $S = -\left( \frac{\partial F}{\partial T} \right)_{V,N} = N k_B \left[ a \coth a - \ln(a \sinh a) \right]$ & 0 & $S = N k_B \left[ 1 - \ln(\beta \hbar \omega) \right]$
Internal energy & $U_{vib} = -\left( \frac{\partial \ln Z_{vib}}{\partial \beta} \right)_{V,N} = N k_B \left[ \frac{1}{2} + \frac{1}{e^{\hbar \omega / k_B T} - 1} \right]$ & 0 & $2 \times \frac{1}{2} \times N k_B T = nRT$
Pressure & $P = \frac{N}{\beta} \left( \frac{\partial \ln(z)}{\partial V} \right)_{T,N}$ & $N k_B T / V = nRT / V$
Vibrational heat capacity & $C_{vib} = \left( \frac{\partial U_{vib}}{\partial T} \right)_{V,N} = \left( \frac{\partial U_{vib}}{\partial \beta} \right)_{V,N} \left( \frac{\partial \beta}{\partial T} \right)_{V,N}$ & $N k_B \left( \frac{\theta_{vib}}{T} \right)^2 e^{-\theta_{vib} / T} \left( e^{\theta_{vib} / T} - 1 \right)^2$ & $N k_B = nR$

<table>
<thead>
<tr>
<th>Substance</th>
<th>$\theta_{vib} = \frac{\hbar \omega}{k_B}$ (K)</th>
<th>$\theta_{rot} = \frac{\hbar^2}{2 I k_B}$ (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H$_2$</td>
<td>6140</td>
<td>85.4</td>
</tr>
<tr>
<td>O$_2$</td>
<td>2239</td>
<td>2.1</td>
</tr>
<tr>
<td>N$_2$</td>
<td>3362</td>
<td>2.9</td>
</tr>
<tr>
<td>Cl$_2$</td>
<td>810</td>
<td>0.0347</td>
</tr>
</tbody>
</table>

**Example:** If you know that $\hbar \omega = 0.29$ eV for N$_2$, calculate $c_{vib}$ per mole at $T = 1000$ K. [Note: any temperature less than 3362 K, will be in quantum region, $k_B = 1.38 \times 10^{-23}$ J K$^{-1}$]

**Answer:** From the above table, it was found that 1000 K < $\theta_{vib}$ (N$_2$). Consequently, 1000 K will be in the quantum region. Then, use $a = \frac{3362}{1000} = 3.362$

We can have

$$c_{vib} = R \left( \frac{\theta_{vib}}{T} \right)^2 e^{\theta_{vib} / T} \left( e^{\theta_{vib} / T} - 1 \right)^2 = 8.31 \left( \frac{a^2}{e^a - 1} \right) = 3.49 \text{ J mole}^{-1} \text{ K}^{-1}$$

This is in excellent agreement with the experimental value, 3.43 J mole$^{-1}$ K$^{-1}$, and away from the classical value $c_{vib} = R = 8.314$ JK$^{-1}$ mol$^{-1}$. 

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**Rotational modes:**

Classically, the kinetic energy of rotation is:

$$K.E. = \frac{1}{2} I \omega^2 = \frac{(l \omega)^2}{2I} = \frac{L^2}{2I}$$

Using the relation $m_1r_1 = m_2r_2$, $r_o = r_1 + r_2$, then the moment of inertia about an axis through the center of mass of a diatomic molecule is:

$$I = m_1r_1^2 + m_2r_2^2 = \mu r_o^2,$$

$$\mu = \frac{m_1m_2}{m_1 + m_2}$$

The rotational energy level is given by:

$$\varepsilon_l = \frac{L^2}{2I} = \frac{l(l + 1)}{2I} \hbar^2, \quad l = 0, 1, 2, \ldots,$$

Where, $I = \mu r_o^2$, $\mu$ is the reduced mass, $r_o$ is the equilibrium distance between the nuclei, and $I$ is the moment of inertia of the molecule relative to a perpendicular axis passing through the center of mass and $l$ determining the angular momentum of the molecule relative to the center of mass with its degeneracy $g_l = (2l + 1)$.

The partition function:

$$z_{rot} = \sum_l g_le^{-\beta\varepsilon_l} = \sum_l (2l + 1)e^{-\beta\varepsilon_l} = \sum_l (2l + 1)e^{-l(l+1)\theta_{rot}/T}, \quad \theta_{rot} = \frac{\hbar^2}{2Ik_B}$$

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**A- Low temperatures, $T << \theta_{rot}$, we just take the first two terms in the series leading to**

$$z_{rot} = \sum_l (2l + 1)e^{-\beta\varepsilon_l} = 1 + 3e^{-2\theta_{rot}/T},$$

$$U_{rot} = 6Nk_B\theta_{rot}e^{-2\theta_{rot}/T},$$

$$C_{V,rot} = 3Nk_B\left(\frac{2\theta_{rot}}{T}\right)^2 e^{-2\theta_{rot}/T}$$

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**B- High temperatures:** At high temperature, $T >> \theta_{rot}$, a very large number of rotational states are occupied. Also, the spacing of the rotational levels becomes very small compared with the thermal energy, and we may compute $z_{rot}$ by replacing the summation by integration. We also substitute $2l$ for $2l+1$ and $l^2$ for $(l+1)$. Then

$$Z_{rot, classical} \approx \int_0^\infty d(l + 1)e^{-l(l+1)\theta_{rot}/T} \approx \int_0^\infty 2le^{-l^2\theta_{rot}/T} dl = \frac{T}{\theta_{rot}},$$

which leads to internal energy of $Nk_BT$ and a heat capacity of $R$ per mole due to rotations.

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**Example:** Calculate $\theta_{rot}$ for the diatomic nitrogen. [$M = 14.008$ amu]

**Answer:** The mass of a single nitrogen atom is $m = \frac{14.008}{6.023 \times 10^{26}} = 2.325 \times 10^{-26}$ kg, the reduced mass is $\mu = m/2 = 1.163 \times 10^{-26}$ kg, and the moment of inertia of a molecule is

$$I = \mu r_o^2 = 1.163 \times 10^{-26} \text{ kg} \times (1.0976 \times 10^{-10})^2 \text{ m}^2 = 14 \times 10^{-47} \text{ kg.m}^2,$$
\[ \Theta_{\text{rot}} = \frac{\hbar^2}{8\pi^2 I k_B} = \frac{(6.625 \times 10^{-36})^2 \text{J}^2 \text{s}^2}{8\pi^2 \times 14 \times 10^{-47} \text{kg.m}^2 \times 1.38 \times 10^{-23} \text{J} \text{molecule.K}} = 2.88 \text{ K} \]

**Example**: Calculate the partition function for the hydrogen molecule at 300 K, given that the moment of inertia for molecule is \( I = 6.29 \times 10^{-48} \text{ kg.m}^2 \).

**Answer**:

a) Using the classical expression:

\[ z_{\text{rot.classical}} = \frac{T}{\Theta_{\text{rot}}} = \frac{300}{2.88} = 64.03 \]

b) Using the quantum expression

\[ z_{\text{rot, quantum}} = \sum_{l=0}^{\infty} (2l+1)e^{-l(l+1)\Theta_{\text{rot}}/T} \]

One finds:

\[ z_{\text{rot}} = 1.000 + 3e^{-2 \times 64.03/300} + 5e^{-6 \times 64.03/300} + \cdots \]

= 1.000 + 1.958 + 1.389 + 0.540 + 0.126 + \cdots

= 5.001

**Comments**:

1. The contribution due to each rotational level goes through a maximum at \( l = 1 \) and then decay rapidly, becoming negligible by \( l = 6 \).
2. This decreasing is mainly due to the factor \(-l(l+1)\) in the exponent.
3. The difference between the classical and quantum results is due replacing a summation by an integral when quantization is still significant at this temperature.

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**15.6** Use the data of Table 15.1 to determine \( r_o \), the equilibrium distance between the nuclei, for

(a) an \( \text{H}_2 \) molecule;
(b) a \( \text{CO} \) molecule.

**Answer**:

\[ \Theta_{\text{rot}} = \frac{\hbar^2}{2Ik} \quad \text{, where} \quad I = \mu r_0^2 \quad \text{and} \quad \mu \text{ is the reduced mass,} \quad \mu = \frac{m_1 m_2}{m_1 + m_2} \]

Then, \( \Theta_{\text{rot}} = \frac{\hbar^2}{2\mu r_0^2 k} \quad \text{and} \quad r_0 = \frac{\hbar}{\sqrt{2\mu k \Theta_{\text{rot}}}} \)

a) For \( \text{H}_2 \), \( \mu = \frac{m}{2} \), so \( r_0 = \frac{\hbar}{\sqrt{mk \Theta_{\text{rot}}}} \)
Then, \( r_0 = \frac{1.054 \times 10^{-34} \text{ J} \cdot \text{s}}{\sqrt{(1 \text{ amu})(1.66 \times 10^{-27} \text{ kg/amu})(1.38 \times 10^{-23} \text{ J/K})(85.4 \text{ K})}} \)

\( r_0 = 7.54 \times 10^{-11} \text{ m} = 0.754 \text{ Å} \)

b) For CO, \( \mu = \frac{m_1m_2}{m_1 + m_2} = \frac{(12 \text{ amu})(16 \text{ amu})}{12 \text{ amu} + 16 \text{ amu}} = 6.857 \text{ amu} \)

Then, \( r_0 = \frac{\hbar}{\sqrt{2\mu k\theta_{rot}}} = \frac{1.054 \times 10^{-34} \text{ J} \cdot \text{s}}{\sqrt{2(6.857 \text{ amu})(1.66 \times 10^{-27} \text{ kg/amu})(1.38 \times 10^{-23} \text{ J/K})(2.8 \text{ K})}} \)

\( r_0 = 1.12 \times 10^{-10} \text{ m} = 1.12 \text{ Å} \)

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**Summary**

The single particle partition function

\[
E = E_{\text{trans}} + E_e + E_{\text{rot}} + E_{\text{vib}}
\]

\[
E = E_{\text{trans}} + E_e >> E_{\text{vib}} >> E_{\text{rot}}
\]

\[
z = z_e \times z_{\text{rot}} \times z_{\text{vib}} = V\left(\frac{2\pi m}{\hbar^2}\right)^{3/2} \times z_e \times z_{\text{rot}} \times z_{\text{vib}}
\]

\[
C_V = C_{V,e} + C_{V,\text{rot}} + C_{V,\text{vib}}
\]

\[
C_V = 3 \left(\frac{1}{2}Nk_B\right) + 2 \left(\frac{1}{2}Nk_B\right) + 2Nk_B \left[\frac{1}{2}\left(\frac{\theta_{\text{vib}}}{T}\right)^2 \left(\frac{e^{\theta_{\text{vib}}/T}}{e^{\theta_{\text{vib}}/T} - 1}\right)^2\right]
\]

**Note:** Regarding \( C_V \), \( C_{V,e} \) will be neglected at low temperature, because the energy difference \( E_e >> E_{\text{vib}} >> E_{\text{rot}} \).

**The total heat capacity**

\[
C_V = C_{V,e} + C_{V,\text{rot}} + C_{V,\text{vib}}
\]

\[
C_V = \frac{3}{2}Nk_B + Nk_B + Nk_B \left(\frac{\theta_{\text{vib}}}{T}\right)^2 \left(\frac{e^{\theta_{\text{vib}}/T}}{e^{\theta_{\text{vib}}/T} - 1}\right)^2
\]

For most diatomic molecules the separation between the rotational energy levels is much less than \( k_B T_{\text{room}} \), but the separation between vibrational levels is much greater than \( k_B T_{\text{room}} \). This means that the heat capacity at room temperature is typically \( 5R/2 \) per mole; with \( 3R/2 \) coming from the translational heat capacity and the other \( R \) from the rotations. At room temperature the vibrational contributions are small, only coming into play at higher temperature.

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**Figure 15.5** Values of \( C_V/nR \) for hydrogen (H\(_2\)) as a function of temperature. The temperature scale is logarithmic. (Adapted from *Thermodynamics, Kinetic Theory, and Statistical Thermodynamics*, 3rd edition, by F.W. Sears and G.L. Salinger, Addison-Wesley, 1975.)
Appendix

Simple Harmonic Oscillator

Consider a one dimensional harmonic oscillator with mass \( m \) and frequency \( \nu \).

a) Write down the Hamiltonian.

b) Use the vibrational energy

\[ E_n = (n + \frac{1}{2})\hbar \nu, \quad n = 0, 1, 2, \ldots \]

to calculate the classical partition function.

c) Calculate the quantum partition function. Show that in the limit of \( \frac{\hbar \nu}{k_B T} \to 0 \) this result reduces to that found classically in part (b).

d) Use the quantum mechanical partition function to calculate the internal energy, entropy, and the heat capacity of a system consisting of \( N \) such oscillator as a function of temperature.

Answer:

a) In one dimension, the Hamiltonian of the system is given by:

\[ \hat{H}(p_x, q_x) = \frac{\hat{p}_x^2}{2m} + \frac{1}{2} m \omega^2 \hat{q}_x^2, \quad \omega = 2\pi \nu \]

b) Classically the partition function for single oscillator is:

\[
Z_{\text{sp}} = Z_{\text{trans}} Z_{\text{vibr}} = \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} e^{-\beta H} \frac{dp_x dq_x}{h} = \frac{1}{h} \int_{-\infty}^{\infty} e^{-\frac{\beta p_x^2}{2m}} \int_{-\infty}^{\infty} e^{-\frac{\beta m \omega^2 q_x^2}{2}} dx
\]

\[
= \frac{1}{h} \sqrt{\frac{2\pi m}{\beta}} \sqrt{\frac{2\pi}{\beta m \omega^2}} = \frac{1}{\beta \hbar \omega}, \quad \hbar = \frac{h}{2\pi}
\]

Consequently, for \( N \)-oscillator system we get

\[ Z_N = (Z_{\text{sp}})^N = \left( \frac{1}{\beta \hbar \omega} \right)^N 
\]

\[ F = -k_B T \ln Z_N = k_B T \ln (\beta \hbar \omega) \]

H.W. prove the following thermodynamic quantities

\[ \mu = k_B T \ln (\beta \hbar \omega) \]

\[ P = 0 \]

\[ S = Nk_B \left[ \ln (\beta \hbar \omega) + 1 \right] \]

\[ U = Nk_B T = 2 \left( \frac{1}{2} Nk_B T \right) \quad \text{(Equipartition theorem)} \]

\[ C_p = C_v = \left( \frac{\partial U}{\partial T} \right)_{N,Y} = Nk_B \]

c) In quantum mechanics, since the energy levels is \( E_n = (n + \frac{1}{2})\hbar \nu \), the partition function is given by
In the limit \( a \to 0 \Rightarrow e^a - e^{-a} = (1 + a + \cdots) - (1 - a + \cdots) = 2a = \beta \hbar \omega \), then \( Z_\varphi = \frac{1}{\beta \hbar \omega} \), which is the same result as in part b.

d) For \( N \)-independent particles

\[
Z_N = (Z_\varphi)^N = (2 \sinh a)^N
\]

Writing \( \beta = 1/k_B T \) we could obtain the following results:

\[
F = -k_B T \ln Z_N = N k_B T \ln (2 \sinh a) = N k_B T \ln \left( \frac{e^a}{1 - e^{-2a}} \right) = N k_B T \left[ a + \ln \left( 1 - e^{-2a} \right) \right]
\]

\[
U = -\frac{\partial}{\partial \beta} \ln Z = N \left( \frac{\hbar \omega}{2} \right) \coth a = N \left[ \frac{1}{2} \hbar \omega + \frac{\hbar \omega}{e^{2a} - 1} \right]
\]

\[
C_p = C_v = \left( \frac{\partial U}{\partial T} \right)_{N,V} = N k_B \left( e^{2a} \right) \left( e^{2a} - 1 \right)^2 \left( 2a \right)^2
\]

\[
S = \frac{U - F}{T} = N k_B \left[ a \coth a - \ln(2 \sinh a) \right]
\]

H.W. prove that in the limit of \( a \to 0 \) the internal energy will be: \( U = \frac{1}{2} \hbar \omega + 2 \left( \frac{1}{2} N k_B T \right) \).

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15-9. Using the relation

\[
P = N \frac{1}{\beta} \left( \frac{\partial \ln Z}{\partial V} \right)_{T,N}
\]

show that the equation of state of a diatomic gas is the same as that of a monatomic gas.

Answer:

\[
P = N k_B T \left( \frac{\partial \ln Z}{\partial V} \right)_T
\]

Where \( Z = Z_{\text{trans}} Z_{\text{rot}} Z_{\text{vib}} \), so \( \ln Z = \ln Z_{\text{trans}} + \ln Z_{\text{rot}} + \ln Z_{\text{vib}} \).

\( Z_{\text{rot}} \) and \( Z_{\text{vib}} \) do not depend on volume, so \( P = N k_B T \left( \frac{\partial \ln Z}{\partial V} \right)_T = N k_B T \left( \frac{\partial \ln Z_{\text{trans}}}{\partial V} \right)_T \).

\( Z_{\text{trans}} = V \left( \frac{2 \pi m k T}{h^2} \right)^{3/2} \), so \( \ln Z_{\text{trans}} = \ln V + \frac{3}{2} \ln \left( \frac{2 \pi m k T}{h^2} \right) \)

\[
P = N k_B T \left( \frac{\partial \ln Z_{\text{trans}}}{\partial V} \right)_T = N k_B T \left( \frac{\partial \ln V}{\partial V} \right)_T = N k_B T \frac{V}{V} \cdot \text{So, } PV = N k_B T
\]