Velocity distribution of ideal gas molecules

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Review of the distribution of the velocity of a molecule in ideal gas.
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Boltzmann distribution of the state of a system.
Contents

- Review of the distribution of the velocity of a molecule in ideal gas.
- Boltzmann distribution of the state of a system.
- Boltzmann distribution of the configuration of a system.
Time slots

- Tutorial starts from week 3 (28AUG-1SEP).
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- Group A(30%): week 4, 8,12, Mon; group B(70%): week 6,10, 12, Wed.
Consider a polymer molecule consisting of $N$ straight segments. Each segment has a length $\overrightarrow{b}$ and can point to any direction with equal probability. Please show

\[ \overrightarrow{r}_N - \overrightarrow{r}_0 = \sum_{i=1}^{N} \overrightarrow{b}_i; \]

Please show

\[ (\overrightarrow{r}_N - \overrightarrow{r}_0)^2 = \sum_{i,j=1}^{N} \overrightarrow{b}_i \cdot \overrightarrow{b}_j. \]

Please find the solution to $< \overrightarrow{r}_N - \overrightarrow{r}_0 >$.

Please find the solution to $(< \overrightarrow{r}_N - \overrightarrow{r}_0 >)^2$. 
Maxwell distribution of the velocity of ideal gas molecules

- Velocity distribution of one molecule:
  \[ \rho(\vec{v}) = \left( \frac{m}{2\pi k_B T} \right)^{3/2} e^{-\frac{mv^2}{2k_B T}}, \text{ where } v^2 = v_x^2 + v_y^2 + v_z^2. \]

- Speed distribution of one molecule:
  \[ \rho(u) = 4\pi \left( \frac{m}{2\pi k_B T} \right)^{3/2} u^2 e^{-\frac{mu^2}{2k_B T}}. \]

- The joint distribution of the system of \( N \) molecules:
  \[ \rho(\vec{v}_1, \vec{v}_2, \cdots, \vec{v}_N) = \rho(\vec{v}_1)\rho(\vec{v}_2) \cdots \rho(\vec{v}_N) = \left( \frac{m}{2\pi k_B T} \right)^{3N/2} e^{-\frac{m(v_1^2 + v_2^2 + \cdots + v_N^2)}{2k_B T}}. \]
The velocity distribution of a tank of ideal gas is

\[ \rho( \vec{v}_1, \vec{v}_2, \cdots, \vec{v}_N ) = \left( \frac{m}{2\pi k_B T} \right)^{3N/2} e^{-\frac{m(v_1^2 + v_2^2 + \cdots + v_N^2)}{2k_B T}}. \]

It can be rewritten as:

\[ \rho( \vec{v}_1, \vec{v}_2, \cdots, \vec{v}_N ) = \left( \frac{m}{2\pi k_B T} \right)^{3N/2} e^{-\frac{\epsilon_{k,1} + \epsilon_{k,2} + \cdots + \epsilon_{k,N}}{k_B T}} = \left( \frac{m}{2\pi k_B T} \right)^{3N/2} e^{-\frac{E_{\text{total}}}{k_B T}}. \]

Can we generalize the argument to \( \rho(\text{state}) \propto e^{-\frac{E_{\text{state}}}{k_B T}} \)?
Specify the "state" of a freely moving molecule

- The state of a molecule in the tank is specified by its location $\mathbf{r}$ and velocity $\mathbf{v}$. Once ($\mathbf{r}$, $\mathbf{v}$) are specified, the movement of the molecule is determined.

- Because the molecule is freely moving around, $\rho(\mathbf{r}) = 1/V$, where $V$ is the volume.

- Because the position of the molecule and its velocity is uncorrelated, $\rho(\mathbf{r}, \mathbf{v}) = \rho(\mathbf{r}) \times \rho(\mathbf{v}) = \frac{1}{V} \left( \frac{m}{2\pi k_B T} \right)^{3/2} e^{-\frac{mv^2}{2k_B T}}$. 

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Specify the "state" of a tank of ideal gas

- The state of a tank of gas is specified by specifying the position and the velocity of each individual molecules \((\vec{r}_i, \vec{v}_i)\).

- The distribution of the state of a tank of ideal gas is thus:

\[
\rho(\vec{r}_1, \vec{r}_2, \cdots, \vec{r}_N; \vec{v}_1, \vec{v}_2, \cdots, \vec{v}_N) = \frac{1}{V^N \left( \frac{m}{2\pi k_B T} \right)^{3N/2}} e^{-\frac{(\epsilon_{k,1}^2 + \epsilon_{k,2}^2 + \cdots + \epsilon_{k,N}^2)}{k_B T}} = \frac{1}{V^N \left( \frac{m}{2\pi k_B T} \right)^{3N/2}} e^{-\frac{E_{\text{total}}}{k_B T}}
\]
Boltzmann distribution of the "state" of a tank of gas

- The generalization of
  \[
  \rho(\vec{r}_1, \vec{r}_2, \cdots, \vec{r}_N; \vec{v}_1, \vec{v}_2, \cdots, \vec{v}_N) \propto e^{-\frac{E_{\text{state}}(\vec{r}_1, \vec{r}_2, \cdots, \vec{r}_N; \vec{v}_1, \vec{v}_2, \cdots, \vec{v}_N)}{k_B T}}
  \]
  is true for any systems!
- It is called the "Boltzmann distribution"!
- Ideal gas is the simplest example of the General distribution!
Boltzmann distribution of the "configuration state" of a system-a

- The "state" \( (\vec{r}_i, \vec{v}_i) \) we discussed before denotes the absolute state of the system. Once it is specified, the system’s state is uniquely specified, and according to Newton’s 2nd law, the future movement of the system is determined.

- In biology, we are more interested in the configuration state \( \vec{r}_i \), because the interactions among the molecules depend on the configuration of a system.

- can we have \( \rho_s \propto e^{-\frac{E_s}{k_BT}} \), where \( E_s \) is the total interaction energy among the molecules in the configuration state "s"?
Boltzmann distribution of the "configuration state" of a system - b

We know that: the total kinetic energy is \( E_k = \sum_{i=1}^{N} \frac{1}{2} m \vec{v}_i^2 \), the total interaction is \( E_s = \sum_{i<j} \phi(\vec{r}_j - \vec{r}_i) \), and the total energy of the state is \( E_{state} = E_k + E_s \).

We know that \( \rho(\vec{r}_1, \vec{r}_2, \cdots, \vec{r}_N; \vec{v}_1, \vec{v}_2, \cdots, \vec{v}_N) \propto e^{-\frac{E_{state}(\vec{r}_1, \vec{r}_2, \cdots, \vec{r}_N; \vec{v}_1, \vec{v}_2, \cdots, \vec{v}_N)}{k_B T}} = e^{-\frac{E_k(\vec{v}_1, \vec{v}_2, \cdots, \vec{v}_N)}{k_B T}} e^{-\frac{E_s(\vec{r}_1, \vec{r}_2, \cdots, \vec{r}_N)}{k_B T}} \).

We know the configuration distribution: \( \rho(\vec{r}_1, \vec{r}_2, \cdots, \vec{r}_N) = (\int d\vec{v}_1 \int d\vec{v}_2 \cdots \int d\vec{v}_N \rho(\vec{r}_1, \vec{r}_2, \cdots, \vec{r}_N; \vec{v}_1, \vec{v}_2, \cdots, \vec{v}_N) \propto (\int d\vec{v}_1 \int d\vec{v}_2 \cdots \int d\vec{v}_N e^{-\frac{E_k(\vec{v}_1, \vec{v}_2, \cdots, \vec{v}_N)}{k_B T}}) e^{-\frac{E_s(\vec{r}_1, \vec{r}_2, \cdots, \vec{r}_N)}{k_B T}} \).
The normalization factor of the Boltzmann distribution of the "configuration state" of a system

- So we do have \( \rho_s(\vec{r}_1, \vec{r}_2, \cdots, \vec{r}_N) = (Z)^{-1} e^{-\frac{E_s(\vec{r}_1, \vec{r}_2, \cdots, \vec{r}_N)}{k_B T}} \).

- The quantity \( Z \) is determined by:

\[
Z = \int d\vec{r}_1 d\vec{r}_2, \cdots, d\vec{r}_N e^{-\frac{E_s((\vec{r}_1, \vec{r}_2, \cdots, \vec{r}_N))}{k_B T}}.
\]

Obviously, \( Z^{-1} \) is the normalization factor.

- \( Z \) is called the partition function. It contains important information of the system. We will discuss the importance of \( Z \) in the future classes.
Example 0: one free particle system in 1-d box of size \( L \)

- Its configuration state is specified by its coordinate \( x \).
- It is a free particle, so no interaction, \( E_s(x) = 0 \).
- The partition function \( Z = L \), and the distribution is \( \rho(x) = 1/L \).
Example 1: one harmonically bound particle system in 1-d

Now let’s consider that the particle is bound to the center by a spring, so \( E_s(x) = \frac{1}{2} k x^2 \), where \( k \) is the force constant of the spring, and \(-\frac{L}{2} < x < \frac{L}{2}\).

\[
Z = \int_{-L/2}^{L/2} e^{-\frac{1}{2} k x^2 / k_B T} \approx \int_{-\infty}^{\infty} e^{-\frac{1}{2} k x^2 / k_B T} = \sqrt{\frac{2 \pi k_B T}{k}}.
\]

\[
\rho(x) = \sqrt{\frac{k}{2 \pi k_B T}} e^{-\frac{k x^2}{2 k_B T}}.
\]

\[
\sigma^2 = \frac{k_B T}{k} . \quad P(-\sigma < x < \sigma) = ?
\]
Example 2: one trapped particle system in 1-d

Now let’s consider that the particle is bound to the center by a short range interaction, so \( E_s(x) = -\epsilon \) when \(-d/2 < x < d/2\), and \( E_s(x) = 0 \) when \( x < -d/2 \) or \( x > d/2 \).

\[
Z = \int_{-L/2}^{-d/2} dx 1 + \int_{-d/2}^{d/2} dx e^{-\frac{E_s(x)}{k_B T}} + \int_{d/2}^{L/2} dx 1 = L - d + de^{\frac{\epsilon}{k_B T}}.
\]

\[
\rho(x) = \frac{1}{L-d(1-e^{\frac{\epsilon}{k_B T}})} e^{-\frac{E_s(x)}{k_B T}}.
\]

\[
P_{\text{trap}} = \int_{-d/2}^{d/2} dx \rho(x) = \frac{de^{\frac{\epsilon}{k_B T}}}{L-d(1-e^{\frac{\epsilon}{k_B T}})} = \frac{\gamma e^{\frac{\epsilon}{k_B T}}}{1-\gamma(1-e^{\frac{\epsilon}{k_B T}})}, \text{ where}
\]

\[
\gamma = \frac{d}{L}.
\]
Example 2: continue

\[ f_s(x) = \begin{cases} \frac{d}{2} < x < \frac{d}{2} \\ 0, \quad x < \frac{d}{2}, \text{ or } x > \frac{d}{2} \end{cases} \]

\[ \int_{-d/2}^{d/2} P(x) \, dx = ? \]

\[ P_{\text{trap}} = \int_{-d/2}^{d/2} P(x) \, dx = ? \]

\[ P_{\text{trap}} / P_{\text{free}} = ? \]
Example 2: continue

\[ \rho(x) = \frac{1}{L-d(1-e^{-\frac{E_s(x)}{k_B T}})} e^{-\frac{E_s(x)}{k_B T}} \]

\[ C = \frac{1}{L-d(1-e^{-\frac{E_s(x)}{k_B T}})} \]

\[ P_{\text{trap}} = d \cdot \frac{1}{L-d(1-e^{-\frac{E_s(x)}{k_B T}})} e^{\frac{E_s}{k_B T}} \]

\[ = \frac{\gamma}{1-\gamma(1-e^{-\frac{E_s}{k_B T}})} e^{\frac{E_s}{k_B T}} ; \quad \gamma = \frac{d}{L} \]

\[ P_{\text{free}} = (L-d) \cdot \frac{1}{L-d(1-e^{-\frac{E_s}{k_B T}})} = \frac{1-\gamma}{1-\gamma(1-e^{-\frac{E_s}{k_B T}})} \]

\[ \frac{P_{\text{trap}}}{P_{\text{free}}} = \frac{\gamma}{1-\gamma} e^{\frac{E_s}{k_B T}} \]
Example 2: continue

- $\rho(x) = ?$ for $\epsilon \to \infty$.
- $\rho(x) = ?$ for $\epsilon \to -\infty$.
- $\rho(x) = ?$ for $\epsilon \to 0$.
- $\rho(x) = ?$ for $T \to \infty$.
- $\rho(x) = ?$ for $T \to 0$.
- $\rho(x) = ?$ for $\gamma \to 0$.
- $\rho(x) = ?$ for $\gamma \to 1$. 

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Example 2: one trapped particle system in 1-d continue

- Re-understanding: \( P_{\text{trap}} = \frac{d e^{\epsilon / k_B T}}{L - d(1 - e^{\epsilon / k_B T})} = \frac{n e^{\epsilon / k_B T}}{(N - n) + n e^{\epsilon / k_B T}} \), where \( N = L / l \), \( n = d / l \), while \( l \) is the occupation length (the size) of the particle.

- Re-understanding of two region binding problem:

\[
P_i = \frac{n_i e^{\epsilon_i / k_B T}}{n_2 e^{\epsilon_2 / k_B T} + n_1 e^{\epsilon_1 / k_B T}},
\]

where \(-\epsilon_i\) is the interaction energy of the particle in region \( i \), and \( n_i \) is the number of rooms in region \( i \). The previous example corresponds to \( \epsilon_1 = \epsilon \), and \( \epsilon_2 = 0 \). Show that \( P_1 + P_2 = 1 \), and \( P_1 / P_2 = \frac{n_1}{n_2} e^{\frac{\epsilon_1 - \epsilon_2}{k_B T}} \).