An alternative expression to the Sackur-Tetrode entropy formula for an ideal gas

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Abstract

An expression for the entropy of a monoatomic classical ideal gas is known as the Sackur-Tetrode equation. This pioneering investigation about 100 years ago incorporates quantum considerations. The purpose of this paper is to provide an alternative expression for the entropy in terms of the Heisenberg uncertainty relation. The analysis is made on the basis of fluctuation theory, for a canonical system in thermal equilibrium at temperature \( T \). This new formula indicates manifestly that the entropy of macroscopic world is recognized as a measure of uncertainty in microscopic quantum world. The entropy in the Sackur-Tetrode equation can be re-interpreted from a different perspective viewpoint. The emphasis is on the connection between the entropy and the uncertainty relation in quantum consideration.

1. Introduction

The entropy of a monoatomic classical ideal gas has been given independently by the Sackur [1,2] and Tetrode [3,4], which is known as Sackur-Tetrode equation (ST-equation). This is a pioneering investigation about 100 years ago which incorporates quantum considerations. This entropy \( S \) at temperature \( T \) can be written as

\[
\frac{S}{Nk_B} = \frac{5}{2} + \ln \left( \frac{V}{N} \left( \frac{2\pi m k_B T}{\hbar^2} \right)^{3/2} \right),
\]

which shows a fundamental step towards modern physics. Here \( N \) is the number of particles in the gas, \( k_B \) is Boltzmann's constant, \( V \) is the volume of the gas, \( m \) is the mass of a gas particle and \( \hbar \) is Planck's constant. The detailed explanation and summary for the derivation of the ST-equation is described in a textbook [5].

Experimental verification and validity of this equation is not easy because the ideal gas does not exist indeed, and real gas becomes condensed state at low temperature. Experimental measurements and analyses are carried out for Ne, Ar, Kr and Hg, with a calorimetric method. Their vapors are monoatomic and behave in good approximation as ideal gases in gaseous phase. These experimental analyses, taking into account the corrections caused from the difference between the real monoatomic gases and the ideal gas, are described in detail in Ref. [6]. The experimental justification and correctness of the ST-equation has been inferred.

The almost forgotten episode for the physics of derivation of the ST-equation is highlighted in a recent paper "On the 100th anniversary of Sackur-Tetrode equation" by W. Grimus [7]. He emphasizes that the charm of the ST-equation has not changed over 100 years, which never fades away timelessly, and its importance in development of quantum theory and statistical mechanics.

What kind of re-interpretation for the ST-equation is possible? Is it really possible to add new explanation for entropy? This paper intends to provide an alternative expression for the entropy of a monoatomic classical ideal gas. Consequently, the entropy of a classical ideal gas can be written in terms of the thermal uncertainty relation based on the Heisenberg uncertainty relation. The key issue is to introduce the thermal uncertainty relation, which will be defined below.

2. General remarks on the Sackur-Tetrode equation and a possible extension

In the derivation of ST-equation, the following two conditions (a) and (b) are considered in the context the quantum nature.

(a) The entropy is obtained by the Boltzmann relation \( S = k_B \ln W \), where \( W \) is the number of accessible microscopic states and \( k_B \) is the Boltzmann's constant. In order to count the number of microscopic possible states \( W \), Sackur and Tetrode have introduced the elementary cell or domain in phase space of position and momentum. In this way, the
The entropy is a measure of the uncertainty. The calculations to derive Eq. (2) are primitive, using elementary mathematics. Since the context of the story must be clear, each small step on the calculations will be provided with sufficient details for better understanding.

\[ S = \text{constant} + \ln \left( \frac{((\Delta x)_r(\Delta p)_r)^2}{\hbar^4N} \right). \]  

(2)

3. Results and discussion

3.1. Uncertainty relation in a potential well

For the particle trapped between rigid walls in one-dimension the quantized energy is

\[ \varepsilon_n = \frac{\hbar^2}{8mL^2} n^2 = an^2, \quad a = \frac{\hbar^2}{8mL^2}, \quad n = 1, 2, 3, \ldots, \]  

(3)

where \( m \) is the mass of a gas particle, \( L \) is the length of the well in a linear dimension.

The energy \( \varepsilon_0 = 0 \) is not permitted, that is, the particle cannot be at rest between the rigid walls. The wave functions in \(-L/2 < x < L/2\) are given by

\[ \varphi_n = \sqrt{\frac{2}{L}} \cos \left( \frac{n \pi x}{L} \right), \quad n = 1, 3, 5, \ldots, \]  

(4)

\[ \varphi_n = \sqrt{\frac{2}{L}} \sin \left( \frac{n \pi x}{L} \right), \quad n = 2, 4, 6, \ldots, \]  

(5)

Since \( \langle \varphi_m|x|\varphi_n \rangle \) are odd functions, one has simply

\[ \langle n|x|n \rangle = \langle \varphi_n|x|\varphi_n \rangle = 0, \quad n = 1, 2, 3, 4, \ldots. \]

Next, one obtains

\[ \langle n|x^2|n \rangle = \langle \varphi_n|x^2|\varphi_n \rangle = \frac{2}{L} \int_{-\frac{L}{2}}^{\frac{L}{2}} x^2 \cos^2 \left( \frac{n \pi x}{L} \right) dx, \quad n = 1, 3, 5, \ldots. \]  

(6)

\[ \langle n|x^2|n \rangle = \frac{2}{L} \int_{-\frac{L}{2}}^{\frac{L}{2}} x^2 \sin^2 \left( \frac{n \pi x}{L} \right) dx, \quad n = 2, 4, 6, \ldots. \]

Hence the dispersion in position \( \langle \Delta x \rangle^2 \) becomes

\[ \langle n|\langle \Delta x \rangle^2|n \rangle = \langle \langle n|x^2|n \rangle - \langle n|x|n \rangle^2 \rangle, \]

\[ = \langle n|x^2|n \rangle, \]

\[ = \frac{L^2}{12} \left( 1 - \frac{6}{n^2\pi^2} \right), \quad n = 1, 2, 3, 4, \ldots. \]

The root-mean-square fluctuation, \( \langle \Delta x \rangle_n \), in its position is given by

\[ \langle \Delta x \rangle_n = \sqrt{\frac{\langle n|\langle \Delta x \rangle^2|n \rangle \rangle}{n}} = \sqrt{\frac{3}{6}} \frac{L}{\sqrt{1 - \frac{6}{n^2\pi^2}}}, \quad n = 1, 2, 3, 4, \ldots. \]  

(7)

Then the uncertainty in the position of the particle is proportional to the width of the well for any eigenstate of energy.

On the other hand, the eigenvalue of the energy can be written as

\[ \varepsilon_n = \frac{\hbar^2}{8mL^2} n^2 = an^2 = \frac{1}{2m} \langle n|p_x^2|n \rangle, \quad a = \frac{\hbar^2}{8mL^2}. \]  

(8)

\[ \langle n|p_x^2|n \rangle = \langle \varphi_n|p_x^2|\varphi_n \rangle = 2m(\varepsilon_n), \]

\[ = \frac{\hbar^2}{4L^2} n^2, \quad n = 1, 2, 3, \ldots. \]  

(9)

The expectation value \( \langle n|p_x|n \rangle \) becomes zero for any eigenstate because of symmetry consideration in back and forth motion. Then one has
\[ \langle |n|\langle \Delta p_n \rangle^2 |n\rangle = \langle |n|p_n^2 |n\rangle - \langle |n|p_n |n\rangle^2 \]
\[ = \langle |n|p_n^2 |n\rangle. \]

The root-mean-square fluctuation, \( \langle \Delta p_n \rangle_n \), in the momentum becomes
\[ \langle \Delta p_n \rangle_n \equiv \sqrt{\langle |n|\langle \Delta p_n \rangle^2 |n\rangle} = \frac{\hbar}{2L}n, \quad n = 1, 2, 3 \ldots \quad (10) \]

The uncertainty in the momentum of the particle is inversely proportional to the width of the well. Thus Eqs. (7) and (10) yield
\[ \langle \Delta x_n \rangle_n \langle \Delta p_n \rangle_n \equiv \sqrt{\langle |n|\langle \Delta x_n \rangle^2 |n\rangle \langle |n|\langle \Delta p_n \rangle^2 |n\rangle}, \]
\[ = \frac{\hbar^2}{12} \left( n^2 - \frac{6}{\pi^2} \right) \]
\[ = \frac{\sqrt{3}}{12} \hbar n \sqrt{n^2 - \frac{6}{\pi^2}}, \quad n = 1, 2, 3 \ldots \quad (11) \]

where, for avoiding confusion, the subscript \( n \) in \( \langle \Delta x_n \rangle_n \) and \( \langle \Delta p_n \rangle_n \) indicates a certain quantum eigenstate. It is noted that \( \langle \Delta x_n \rangle_n \) does not depend on the length \( L \). The minimum value occurs when \( n = 1 \), where
\[ \langle \Delta x_1 \rangle \langle \Delta p_1 \rangle = \frac{\sqrt{3}}{12} \hbar n = bn, \quad b = \frac{\sqrt{3} \hbar}{12}, \quad n \gg 1. \quad (12) \]

In this approximation in Eq. (13), the error for the value of \( \langle \Delta x_n \rangle \langle \Delta p_n \rangle \) is estimated to be 0.305% when \( n = 10 \), and less than 0.30% for values of \( n > 10 \).

### 3.2. Thermal average of the uncertainty relation

In sufficiently low density or sufficiently high temperature (classical regime), the quantum distribution laws reduce to the Boltzmann distribution, whether boson or fermion. Hence, in order to calculate the average of the uncertainty, the Boltzmann distribution is applied to the monoatomic classical ideal gas. The canonical ensemble leads to a distribution of the system over possible energy. The partition function, \( Z_s \), of a single particle in one-dimensional model in thermal equilibrium with a heat reservoir at temperature \( T \), is given by
\[ Z_s = \sum_{n=1}^{\infty} e^{-\beta \hbar \omega_n}, \quad \beta = \frac{1}{k_B T}, \]
\[ = \frac{1}{\sqrt{2\pi \hbar \omega}} \int_{0}^{\infty} e^{-\beta \hbar \omega} d\omega = \frac{h^2}{8mL^2}. \quad (14) \]

Next calculations are executed by using approximation of Eq. (13),
\[ \sum_{n=1}^{\infty} \langle \Delta x_n \rangle \langle \Delta p_n \rangle_n e^{-\beta \hbar \omega} = \sum_{n=1}^{\infty} bne^{-\beta \hbar \omega}, \quad b = \frac{\sqrt{3}}{12}, \quad (15) \]
\[ = b \int_{0}^{\infty} ne^{-\beta \hbar \omega} d\omega, \]
\[ = b \frac{1}{2\beta \hbar} = \frac{b \sqrt{3m \hbar L^2}}{3}. \]

Consequently, the thermal uncertainty average of the uncertainty, which is called thermal uncertainty relation in this paper, can be written as
\[ \langle \Delta x \rangle \langle \Delta p \rangle = \frac{1}{Z} \sum_{n=1}^{\infty} \langle \Delta x \rangle \langle \Delta p \rangle_n e^{-\beta \hbar \omega}, \quad (16) \]
\[ = \frac{b}{\pi} \sqrt{\frac{\pi}{\beta \hbar}} - \frac{\sqrt{3}}{6\pi} \sqrt{2\pi m \hbar k_B T \cdot L}, \]
which is rearranged as
\[ \sqrt{2\pi m \hbar k_B T} = \frac{2\pi \sqrt{3}}{1} \langle \Delta x \rangle \langle \Delta p \rangle. \quad (17) \]

It is noticed that \( \langle \Delta x \rangle \langle \Delta p \rangle \) does not include the Planck’s constant \( \hbar \) because of a cancelation of \( \hbar \) in the calculations of Eq. (16). This relation (17) breaks down at low temperature. In particular for \( T = 0 \), \( \langle \Delta x \rangle \langle \Delta p \rangle \) in the ground state is not zero because of the zero-point energy, as shown in Eq. (12).

In addition, the other calculations yield
\[ \langle \Delta x \rangle \langle \Delta p \rangle \times \langle \Delta x \rangle \langle \Delta p \rangle = \left\{ \frac{1}{2} \sum_{n=1}^{\infty} \langle \Delta x \rangle e^{-\beta \hbar \omega} \right\} \times \left\{ \frac{1}{2} \sum_{n=1}^{\infty} \langle \Delta x \rangle e^{-\beta \hbar \omega} \right\} , \]
\[ = \frac{\sqrt{3}}{6\pi} \sqrt{2\pi m \hbar k_B T \cdot L}. \]

This result agrees with that obtained in Eq. (16).

#### 3.3. Entropy of the ideal gas in a three-dimensional box

Taking into account the indistinguishability of the particle, the partition function \( Z \) for three-dimensional system is given by
\[ Z = \frac{1}{N!} Z_s^N. \quad (18) \]

Here \( Z_s \) is given by Eq. (14) for a single particle, and the factor \( 1/N! \) is necessary to make entropy extensive quantity, avoiding Gibbs paradox. The Helmholtz’s free energy \( F \) is
\[ F = -k_B T \ln Z = -k_B T \ln \left( \frac{1}{N!} Z_s^N \right). \quad (19) \]

By using Eqs. (14) and (18) one then has
\[ Z = \frac{L^N}{N!} \left( \frac{2\pi m \hbar k_B T}{h^2} \right)^{3N/2}. \quad (20) \]

The result can be written with the Stirling’s formula, \( \ln N! = N \ln N - N \),
\[ F / N k_B = -T - T \ln V \left( \frac{3}{2} \ln \left( \frac{2\pi m \hbar k_B T}{h^2} \right) \right) , \quad V = L^3, \quad (21) \]
where \( V \) is the volume of the gas.

The entropy, \( S \), is derived from \( F \) in the forms
\[ S = -\left( \frac{\partial F}{\partial T} \right)_V , \quad (22) \]
\[ S = \frac{5}{2} + \ln V + \frac{3}{2} \ln \left( \frac{2\pi m \hbar k_B T}{h^2} \right) . \quad (23) \]

These Eqs. (22) or (23) are the so-called Sackur-Tetrode equation, which is the same given in Eq. (1). When the extensive valuables \( V \) and \( N \) are multiplied by 2, the entropy is multiplied by 2. Formally : \( S(T, 2V, 2N) = 2S(T, V, N) \) is satisfied, hence the entropy is satisfied with an extensive quantity. When the logarithm term decreases below \(-5/2\), the entropy becomes negative. Hence the Eq. (23) is appropriate approximation when the argument of the logarithm is much higher than unity.
Now let us consider the thermal uncertainty relation in order to connect the ST-equation. From Eq. (17), one has

\[ |(\Delta x) (\Delta p_x) (\Delta p_y) (\Delta p_z)| = \sqrt{\frac{3}{2}} \sqrt{2 \pi n k_B T} \frac{V}{h^3}, \quad V = L^3. \tag{24} \]

In this way, the magnitude of \(|(\Delta x) (\Delta p_x) (\Delta p_y) (\Delta p_z)|\) is proportional to \(T^{3/2} V\). Using Eqs. (17), (21), and (22), \(F\) and \(S\) are connected to the thermal uncertainty relation, and given by

\[ \frac{F}{N k_B} = -T - 3T \ln(2\pi \sqrt{3}) + 3 \ln V - 3 \ln \left( \frac{(\Delta x) (\Delta p_x) (\Delta p_y) (\Delta p_z)}{h} \right), \tag{25} \]

\[ \frac{S}{N k_B} = \frac{5}{2} + 3 \ln(2\pi \sqrt{3}) - \ln N + 3 \ln \left( \frac{(\Delta x) (\Delta p_x) (\Delta p_y) (\Delta p_z)}{h} \right), \]

\[ C_1 + \ln \left( \frac{(\Delta x) (\Delta p_x) (\Delta p_y) (\Delta p_z)}{N h^3} \right), \tag{26} \]

\[ C_1 = \frac{5}{2} + 3 \ln(2\pi \sqrt{3}). \]

Substituting Eq. (24) to Eq. (26), the arrangement yields

\[ \frac{S}{N k_B} = C_2 + \ln \left( \frac{V}{N} \left( \frac{2 \pi n k_B T}{h} \right)^3 \right), \quad C_2 = \frac{5}{2} + 2 \ln(\pi). \tag{27} \]

The difference between Eqs. (1) and (27) is \(2 \ln(\pi) = 2.29\), which may arise from the small errors for the approximation in Eq. (13).

The Eq. (26) is equivalently expressed as,

\[ \frac{S}{N k_B} = \text{constant} + \ln \left( \frac{(\Delta x) (\Delta p_x) (\Delta p_y) (\Delta p_z)}{N h^3} \right). \tag{28} \]

This Eq. (28) is the main result in this paper, which shows an alternative expression for the entropy of a monoatomic classical ideal gas. The entropy is regarded as the number of \(h^3\)-elementary cell in the thermal uncertainty volume space \(|(\Delta x) (\Delta p_x) (\Delta p_y) (\Delta p_z)|\) per \(N\). This uncertainty volume space is determined at given temperature. The fundamental concept of entropy is provided from an aspect of uncertainty relation. The entropy specifies manifestly a measure of uncertainty.

Fig. 1 shows the Eq. (28) in graphical representation. It is noted that the value of \(S/N k_B\) becomes negative below 1.0 for the x-axis.

In addition, the internal energy of the gas, \(E\), and the heat capacity at constant volume, \(C_v\), are

\[ E = k_B T \left( \frac{\partial}{\partial T} \ln Z \right)_V = \frac{3}{2} N k_B T, \tag{29} \]

\[ C_v = \frac{\partial E}{\partial V} = \frac{3}{2} N k_B. \]

It is noted that \(E, C_v\), pressure \(P = -(\partial F/\partial V)_T = N k_B T/V\), and heat capacity \(C_p\) at constant pressure, are free from the Planck’s constant \(h\). On the other hand, the Helmholtz’s free energy \(F\) and the entropy \(S\) include the Planck’s constant \(h\).

Another calculation from Eqs. (25) and (26) leads to the same result

\[ E = F + TS = \frac{3}{2} N k_B T, \]

\[ \frac{9 N \pi}{m} \left( \frac{(\Delta x) (\Delta p_x) (\Delta p_y) (\Delta p_z)}{L} \right)^2, \tag{30} \]

\[ k_B T = \frac{6 \pi}{m} \left( \frac{(\Delta x) (\Delta p_x) (\Delta p_y) (\Delta p_z)}{L} \right)^2. \]

This is a connection between internal energy of monoatomic ideal gas and the thermal uncertainty relation.

3.4. The thermal de Broglie wavelength

The de Broglie wavelength \(\lambda_T\), is defined as \[11\]

\[ \lambda_T = \frac{h}{\sqrt{2 \pi n k_B T}}. \tag{31} \]

This wavelength shows the quantum nature of matter, reflecting the wave particle duality. Using the Eqs. (21), (22) and (29), the following expressions are obtained.

\[ E = \frac{3N}{4\pi m} \left( \frac{h}{\lambda_T} \right)^2, \tag{32} \]

\[ \frac{F}{N k_B} = -T + T \ln \left( \frac{N}{V^{3/2}} \right), \quad V = L^3, \tag{33} \]

\[ \frac{S}{N k_B} = \frac{5}{2} + \ln \left( \frac{V}{N \lambda_T^3} \right). \tag{34} \]

The entropy approaches negative infinity as the temperature approaches zero, then this Eq. (34) is valid in the region \(V/N \lambda_T^3 \gg 1\).

The thermal wavelength will be approximately equal to the inter particle distance at \(T\). A linkage between the \(\lambda_T\) and \(|(\Delta x) (\Delta p_x) (\Delta p_y) (\Delta p_z)/h|^3\) has a form

\[ \frac{V}{\lambda_T^3} = (2\pi \sqrt{3})^3 \left( \frac{(\Delta x) (\Delta p_x) (\Delta p_y) (\Delta p_z)}{h} \right)^3. \tag{35} \]

3.5. Comparison with the results of thermodynamics

The entropy \(S\) for the ideal gas in the thermodynamics is given by

\[ dS = \frac{1}{T} dE - \frac{P}{T} dV, \quad E = \frac{3}{2} N k_B T, \tag{36} \]

\[ P = \frac{N k_B}{V}, \quad T = \left( \frac{p^2}{3 m k_B} \right). \]
where \( p^2 \) is the average of momentum of particle. The entropy change between two states \((T, V, N)\) and \((T_0, V_0, N)\) in constant \(N\) is given by

\[
S - S_0 = Nk_B \left[ \frac{3}{2} \ln \frac{T}{T_0} + \ln \frac{V}{V_0} \right],
\]

\[= S_T(\text{momentum}) + S_V(\text{position}). \tag{37}\]

The key point is that the entropy can be decomposed into two contributions, coming from the information of momentum and position. The value of \( S_T \) shows the change of entropy from one momentum distribution to another, in the process of a constant volume. On the other hand, \( S_V \) indicates the entropy change from the volume change at constant temperature. Rearrangement of Eq. (37) leads a form

\[
\frac{S - S_0}{Nk_B} = \ln \left( \frac{T^{3/2}V}{T_0^{3/2}V_0} \right),
\]

\[= \text{constant} + \ln (T^{3/2}V), \tag{38}\]

which corresponds with Eqs. (23) and (28) for the case of constant \(N\). Consequently a relation between the thermodynamic quantities \(V, T\) and the thermal uncertainty relation can be written as

\[
\langle V^{3/2} \rangle = C_3 \langle (\Delta x_i)(\Delta p_i) \rangle^{3/2}, \quad C_3 = \text{constant}. \tag{40}\]

The number 2 in the power of \(T^{3/2}\) is originated from the kinetic energy \(\frac{1}{2}m v^2\) of particle, while the number 3 in both side specifies 3-dimension in model. It is emphasized that Eq. (40) is a kind of bridge equation between macroscopic world in the thermodynamics and microscopic world in the quantum mechanics. The entropy connects clearly to the uncertainty relation from the view point of the thermodynamic aspect.

Fig. 2 shows the variation of the thermal uncertainty relation as a function of temperature.

4. Conclusion

The thermal average of the uncertainty \(\langle \Delta x_i \rangle (\Delta p_i)\) \(T\) has been introduced and given. A new alternative expression for the entropy of a monoatomic classical gas can be written as

\[
S = S_0 + Nk_B \ln \left( \frac{\langle (\Delta x_i)(\Delta p_i) \rangle^{3/2}}{Nh^3} \right) = \text{constant}.
\]

The essential point is to introduce the concept of the thermal uncertainty relation. A bridge between the microscopic Heisenberg uncertainty relation and the entropy in macroscopic world has been provided. Even in thermal equilibrium state, fluctuation, random motion or disorder could originate from the uncertainty relation, giving a deeper insight into the entropy. The author would like to dedicate this expression to O. Sackur and H. Tetrode, for celebrating 100th anniversary of Sackur-Tetrode equation.

Acknowledgement

The author would like to thank Professor W. Grimus for valuable information concerning the Sackur-Tetrode equation.

References