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The Ideal Gas on the Canonical Ensemble

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1. Introduction

We are going to analyze an ideal gas on the canonical ensemble, we will not use quantum mechanics, however, we will need to take account of some quantum effects, and as a result the treatment is a semi-classical treatment. I'm going to take the calculation several steps farther than our author, in particular, I'll derive the ideal gas law.

2. The Ideal Gas

We have already noted that an ideal gas is an idealization in which we can ignore the potential energy terms. That is the interaction energy of the molecules is negligible. This means that we can write the energy of the ideal gas in terms of a sum of energies for each molecule.

The energies

$$\epsilon_1 \leq \epsilon_2 \leq \epsilon_3 \leq \dots \leq \epsilon_r \leq \dots$$

correspond to the complete set of (discrete) quantum states $1, 2, \dots, r, \dots$, in which a single molecule can exist. To analyze this system on the

canonical ensemble, we need to impose the conditions of the canonical ensemble. Accordingly, consider N particles of an ideal gas contained in a volume V in contact with a heat bath at temperature T . We can specify the state of the gas by counting the number of molecules in each quantum state. If we denote the occupancy of the i^{th} state by N_i , then N_i is the occupancy of the i^{th} level. As in our previous example, the energy of the gas is given by

$$E(N_1, N_2, \dots, N_r, \dots) = \sum_r N_r \epsilon_r,$$

the sum being taken over all single particles states. Since we have N particles, we must have

$$N = \sum_r N_r$$

2.1. The Partition Function for the Ideal Gas

There are some points where we need to be careful in this calculation. We can easily calculate the partition function for a single molecule

$$Z(T, V, 1) = Z_1(T, V) = \sum_r e^{-\beta \epsilon_r}.$$

At this point it is tempting to write

$$Z_1^N = Z(T, V, N).$$

Unfortunately, the answer is wrong! Why? We can see why it is wrong by considering two particles.

- **Detailed Calculation for a two particle ideal gas**

Assuming we can write the partition function for an ideal gas as a product of single particle partition functions, for two particles we

would have

$$\left(\sum_s e^{-\beta \epsilon_s} \right) \left(\sum_t e^{-\beta \epsilon_t} \right) = \sum_s e^{-2\beta \epsilon_s} + \underbrace{\sum_s \sum_t}_{(s \neq t)} e^{-\beta(\epsilon_s + \epsilon_t)}$$

The first term on the r.h.s corresponds to all terms on the l.h.s for which both molecules are in the same state, the second term corresponds to the molecules being in different states. We can now see the problem. When the particles are in different state, we have counted each state twice. The state with one molecule in state 1, the other in state 2, could be written as $s = 1, t = 2$ or as $s = 2, t = 1$. Now except for the fact that we've labelled these states as 1 and 2, the two states of the gas are the same. But the molecules are identical, we cannot justify counting the states twice. It only the occupation numbers that matter - we can't distinguish between the states where particle labels are exchanged experimentally. Now, we already know how to delete useless rearrangements – think golfing foursomes – we

divide by the factorial of the number of objects, in this case $2!$. Thus, the correct expression for partition function of the two particle ideal gas is

$$Z(T, V, 2) = \sum_s e^{-2\beta\epsilon_s} + \frac{1}{2!} \underbrace{\sum_s \sum_t}_{(s \neq t)} e^{-\beta(\epsilon_s + \epsilon_t)}.$$

• Generalization to N molecules

For more particles, we would get lots of terms, the first where all particles were in the same state, the last where all particles are in different states, where the last term must be divided by $N!$ to eliminate overcounts. Thus, we should write

$$Z(T, V, N) = \sum_s e^{-N\beta\epsilon_s} + \dots + \frac{1}{N!} \underbrace{\sum_{s_1} \dots \sum_{s_N}}_{\text{all } s_N \text{ different}} e^{-\beta(\epsilon_{s_1} + \dots + \epsilon_{s_N})}$$

In the terms represented by the ellipsis, some particles are in the same states, some particles are in different states and they need to be appropriately weighted. However, it isn't necessary for us to write these terms. In the classical regime, the probability of a single particle state being occupied by more than one particle is vanishingly small. If a few states are doubly or triply occupied, they contribute little to the partition function and can be safely omitted. In fact, we can safely approximate the partition function by the last term in the expression for the partition function.

- **Relationship Between the N-particle and single particle Partition Function**

Thus,

$$Z(T, V, N) = \frac{1}{N!} \left(\sum_r e^{-\beta \epsilon_r} \right)$$

and the relationship between $Z(T, V, N)$ and Z_1 is

$$Z = Z(T, V, N) = \frac{1}{N!} [Z_1(T, V)]^N$$

The division by $N!$ makes this calculation semi-classical. It is often ascribed to the particles being non-localized. If a particle is localized to a site on a crystal lattice, this serves to distinguish that particle and division by $N!$ is not needed.

2.2. Evaluation of the Partition Function

To find the partition function for the ideal gas, we need to evaluate a single particle partition function. To evaluate Z_1 , we need to remember that energy of a molecule can be broken down into internal and external components. The external components are the translational energies, the internal components are rotations, vibrations, and electronic excitations. To represent this we write

$$\epsilon_r = \epsilon_{sj} = \epsilon_s^{\text{tr}} + \epsilon_j^{\text{int}}.$$

In this expression ϵ_s^{tr} is the translational energy, ϵ_j^{int} is the internal energy. We use this to rewrite Z_1 as

$$Z_1 = \sum_r e^{-\beta \epsilon_r} = \sum_s \sum_j e^{-\beta(\epsilon_s^{\text{tr}} + \epsilon_j^{\text{int}})}$$

or

$$Z_1 = \left(\sum_s e^{-\beta \epsilon_s^{\text{tr}}} \right) \left(\sum_j e^{-\beta \epsilon_j^{\text{int}}} \right) = Z_1^{\text{tr}} Z_{\text{int}}$$

where

$$Z_1^{\text{tr}} = Z^{\text{tr}}(T, V, 1) = \sum_s e^{-\beta \epsilon_s^{\text{tr}}}$$

and

$$Z_{\text{int}} = Z^{\text{int}}(T) = \sum_j e^{-\beta \epsilon_j^{\text{int}}}.$$

Again, we see a partition function factorizing, this enables us to evaluate the pieces separately. Z_1 is the same for all gases, only the internal

parts change. For now we'll assume that all internal energies are in the ground state, so $Z_{int} = 1$. So let's evaluate Z_1 .

3. The translational, single-particle partition function

We'll calculate Z_1^{tr} once and for all, the result will apply to all molecules in the classical regime. We know that we can write $\epsilon^{tr} = p^2/2m$, classically E , p can take on any value, quantum mechanically we can still write $\epsilon^{tr} = p^2/2m$, but ϵ^{tr} and p are restricted to discrete values. To address this, we need to introduce the density of states.

3.1. Density of States

Consider a single, spinless particle in a cubical box of side L . We can write

$$\epsilon = \frac{p^2}{2m} = \frac{1}{2m}(p_x^2 + p_y^2 + p_z^2)$$

We (from our knowledge of quantum mechanics) expect it to be represented by a standing wave, in 3 dimensions this is

$$\psi_{n_1, n_2, n_3} = (\text{Constant}) \sin\left(\frac{n_1 \pi x}{L}\right) \sin\left(\frac{n_2 \pi y}{L}\right) \sin\left(\frac{n_3 \pi z}{L}\right)$$

$n_1, n_2, n_3 = 1, 2, 3, \dots$ The solutions vanish at $x, y, z = 0, L$

We then define

$$k^2 = \frac{\pi^2}{L^2} (n_1^2 + n_2^2 + n_3^2)$$

where \vec{k} is the wave vector with components

$$\vec{k} = \left(\frac{\pi n_1}{L}, \frac{\pi n_2}{L}, \frac{\pi n_3}{L} \right)$$

We can plot these vectors in \vec{k} -space – the points at the tips of the vectors fill \vec{k} -space. These points form a cubic lattice with spacing π/L , the volume per point of \vec{k} -space is $(\pi/L)^3$.

How many of the allowed modes have wave vectors between \vec{k} and

$\vec{k} + d\vec{k}$. Since the n_i are zero, k_1, k_2, k_3 are greater than zero. Thus if we imagine the set of points at the tips of the wave vectors centered at the origin forming a sphere, we should only consider the positive octant.

Let number of modes with a wave vectors between \vec{k} and $\vec{k} + d\vec{k}$ be

$$f(k)dk$$

then

$$f(k)dk = \frac{1}{8} \frac{\overbrace{4\pi k^2 dk}^{\text{volume of shell}}}{\underbrace{(\pi/L^3)}_{\text{volume/point}}}$$

and since $V = L^3$

$$f(k)dk = \frac{V k^2 dk}{2\pi^2}.$$

Now $E = h\nu$, so since $p = \frac{E}{c}$, we have

$$p = \frac{E}{c} = \frac{h\nu}{c} = \frac{h}{2\pi} \frac{2\pi\nu}{c} = \frac{\hbar\omega}{c} = \hbar k$$

Thus $p = \hbar k$ and recognizing that particles can be treated as waves, the number of particles with momentum between p and $p + dp$ is

$$\begin{aligned} f(p)dp &= \frac{V(p/\hbar)^2 dp}{2\pi^2 \hbar} \\ &= \frac{V p^2 dp 4\pi}{h^3} \end{aligned}$$

3.2. Use of density of states in the calculation of the translational partition function

Z_1^{tr} is the sum over all translational states. Thus we can rewrite Z_1^{tr} as an integral using the density of states function. Then

$$Z_1^{tr} = \sum_s e^{-\beta \epsilon_s^{tr}}$$

$$= \int_0^{\infty} \frac{V 4\pi p^2 dp e^{-\beta p^2/2m}}{h^3}$$

3.3. Evaluation of the Integral

We have an integral of the form

$$I_n(a) = \int_0^{\infty} x^n e^{-ax^2} dx \quad a > 0$$

where

$$I_0(a) = \int_0^{\infty} e^{-ax^2} dx$$

To evaluate this, let $ax^2 = u^2$ so $\sqrt{ax} = u$ and $du = \sqrt{a}dx$ Thus

$$I_0(a) = \int_0^{\infty} \frac{1}{\sqrt{a}} e^{-u^2} du$$

$$= \frac{1}{2\sqrt{a}} \int_{-\infty}^{\infty} e^{-u^2} du$$

Now

$$\begin{aligned} \left[\int_{-\infty}^{\infty} e^{-u^2} du \right]^2 &= \left[\int_{-\infty}^{\infty} e^{-x^2} dx \right] \left[\int_{-\infty}^{\infty} e^{-y^2} dy \right] \\ &= \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} e^{-(x^2+y^2)} dx dy \end{aligned}$$

To complete the evaluation, we transform to polar coordinates using $x = r \cos \theta$, and $y = r \sin \theta$, $x^2 + y^2 = r^2$, and $dA = r dr d\theta$, and integrate over the entire plane,

$$\left[\int_{-\infty}^{\infty} e^{-u^2} du \right]^2 = \int_0^{\infty} \int_0^{2\pi} e^{-r^2} r dr d\theta$$

$$= 2\pi \int_0^{\infty} e^{-r^2} dr$$

now let $r^2 = \zeta$ and $d\zeta = 2rdr$
and

$$\begin{aligned} \left[\int_{-\infty}^{\infty} e^{-u^2} du \right]^2 &= 2\pi \int_0^{\infty} e^{-\zeta} \frac{d\zeta}{2} \\ &= \pi \int_0^{\infty} e^{-\zeta} d\zeta \\ &= \pi [e^{-\zeta}]_0^{\infty} \\ &= \pi \end{aligned}$$

and

$$\int_0^{\infty} e^{-u^2} du = \sqrt{\pi}$$

and finally

$$I_0(a) = \frac{\sqrt{\pi}}{2\sqrt{a}} = \frac{1}{2} \sqrt{\frac{\pi}{a}}.$$

Similarly

$$\begin{aligned} I_1(a) &= \int_0^{\infty} x e^{-ax^2} dx \\ &= \frac{1}{2a} \int_0^{\infty} e^{-u} du \\ &= \frac{1}{2a} \end{aligned}$$

All other values can be found from these with a recursion relationship arrived at by differentiating $I_n(a)$ w.r.t a . The values of interest to us are:

$$I_2(a) = \frac{1}{4a} \sqrt{\frac{\pi}{a}}$$
$$I_3(a) = \frac{1}{2a^2}$$

3.4. Use of I_2 to evaluate Z_1

$$I_2(a) = \frac{1}{4a} \sqrt{\frac{\pi}{a}}$$

so

$$Z_1^{\text{tr}} = \int_0^\infty \frac{V 4\pi p^2 dp e^{-\beta p^2/2m}}{h^3} = V \left(\frac{2\pi m k T}{h^2} \right)^{\frac{3}{2}}$$

3.5. The Partition Function for N particles

Using our calculations up to this point

$$Z = Z(T, V, N) = \frac{1}{N!} [Z_1(T, V)]^N$$

so

$$Z = \frac{V^N}{N!} \left(\frac{2\pi m k T}{h^2} \right)^{\frac{3N}{2}} (Z_{\text{int}}(T))^N.$$

Now from $F = -kT \ln Z$ we can find all the important properties of an ideal gas.

4. Calculating the Properties of Ideal Gases from the Partition Function

$$F = -kT \ln Z$$

$$F = -NkT \ln \left\{ \frac{eV}{N} \left(\frac{2\pi mkT}{h^2} \right)^{\frac{3}{2}} Z_{\text{int}}(T) \right\}$$

where I have used

$$N! = \left(\frac{N}{e} \right)^N.$$

This result can easily be demonstrated:

$$\ln N! = \ln \left(\frac{N}{e} \right)^N = N(\ln N - \ln e) = N \ln N - N.$$

4.1. The Equation of State

We have characterized an ideal gas as a gas in which $pV = NkT$ and $E = E(T)$. The term $Z_{\text{int}}(T)$ in

$$F = -NkT \ln \left\{ \frac{eV}{N} \left(\frac{2\pi mkT}{h^2} \right)^{\frac{3}{2}} Z_{\text{int}}(T) \right\}$$

refers to a single molecule, it does not depend on V . Thus, we can write

$$F = F_{\text{tr}} + F_{\text{int}}$$

where

$$F_{\text{tr}} = -NkT \ln \left\{ \frac{eV}{N} \left(\frac{2\pi mkT}{h^2} \right)^{\frac{3}{2}} \right\}$$

and

$$F_{\text{int}} = -NkT \ln Z_{\text{int}}(T) = -NkT \ln \left(\sum_j e^{-\beta \epsilon_j^{\text{int}}} \right).$$

Now $F = E - TS$, $dF = -SdT - pdV + \mu dN$ so

$$p = - \left(\frac{\partial F}{\partial V} \right)_{T,N}$$

and

$$F_{\text{tr}} = -NkT \ln \left(\frac{V}{A} \right)$$

where

$$A = \frac{e}{N} \left(\frac{2\pi mkT}{h^2} \right)^{\frac{3}{2}}.$$

Using this, we easily recover the ideal gas equation of state

$$p = - \left(\frac{\partial F}{\partial V} \right)_{T,N} = -(-NkT) \frac{A}{V} \frac{d(V/A)}{dV} = \frac{NkT}{V}$$

and

$$pV = NkT.$$

5. The Classical Regime

As previously noted, the classical regime is the state where most single particle states are unoccupied, a few contain one molecule, and an insignificant number have higher populations.

The probability of a particle being in a translational state s with

energy ϵ_s^{tr} is given by the Boltzmann distribution

$$P_s = \frac{1}{Z_1^{\text{tr}}} e^{-\beta \epsilon_s^{\text{tr}}}.$$

For N molecules, the mean number of molecules in the state s , $\langle N_s \rangle$ is given by

$$\langle N_s \rangle = NP_s$$

for each state s .

For each translational state s , the molecule can be in many different states of internal motion. A sufficient condition for the classical regime to hold is

$$\langle N_s \rangle \ll 1, \text{ for all } s.$$

We can put this in terms of quantities that pertain to the ideal gas. $\langle N_s \rangle = NP_s$ where

$$P_s = \frac{1}{Z_1^{\text{tr}}} e^{-\beta \epsilon_s^{\text{tr}}}.$$

and

$$Z_1^{\text{tr}} = V \left(\frac{2\pi mkT}{h^2} \right)^{\frac{3}{2}}.$$

So

$$\langle N_s \rangle = \left[\frac{N}{V} \left(\frac{h^2}{2\pi mkT} \right)^{\frac{3}{2}} \right] e^{-\beta \epsilon_s^{\text{tr}}} \ll 1.$$

This expression is certainly true as $h \rightarrow 0$, this is in fact the Maxwell-Boltzmann limit. We have developed classical statistical mechanics. Examining the equation shows that it is easier to meet at high temperatures and low particle concentrations. To clarify things even more, let's rewrite the expression in more familiar terms.

5.1. The Classical Regime in terms of the de Broglie wavelength

We know that we can write

$$\lambda_{dB} = \frac{h}{p} = \frac{h}{\sqrt{2m\epsilon^{\text{tr}}}}.$$

We already know that the mean kinetic energy of a gas molecule in the classical gas is

$$\epsilon^{\text{tr}} = \frac{3}{2}kT.$$

So using this, we have

$$\lambda_{dB} = \frac{h}{\sqrt{3mkT}} = \left(\frac{2\pi}{3}\right)^{\frac{1}{2}} \left(\frac{h^2}{2\pi mkT}\right)^{\frac{1}{2}}.$$

So

$$\left[\frac{N}{V} \left(\frac{h^2}{2\pi mkT} \right)^{\frac{3}{2}} \right] \ll 1.$$

can be rewritten as

$$\left(\frac{3}{2\pi} \right)^{\frac{3}{2}} \frac{N}{V} \lambda_{dB}^3 \ll 1.$$

If we let $\ell = (V/N)^{1/3}$ be the mean distance between molecules in our gas, and omit the numerical factors, the condition for the classical regime to hold becomes

$$\lambda_{dB}^3 \ll \ell^3.$$

In other words, the classical regime is when the de Broglie wavelength is small compared to the mean molecular separation. If we take $T = 273\text{ K}$, for Helium with 10^{20} molecules/ cm^3 , $\ell = 2 \times 10^{-7}$ cm, and $\lambda_{dB} = 0.8 \times 10^{-8}$ cm. Under these conditions quantum mechanical effects are negligible.