

On the Momentum Distribution of Molecules of an Ideal Gas

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ABSTRACT. The energy of a gas in an insulated equilibrium is constant which cannot be exceeded by the energy of a molecule. Consequently, the distribution of momentum (velocity) of a molecule cannot be Maxwellian because it admits a molecule to have arbitrarily large energy. Starting with the microcanonical ensemble corresponding to the constant energy, we derive new non-relativistic and relativistic distributions which, in the limiting case of infinitely many molecules, result in the Maxwell and Jüttner distribution, respectively.

PACS number: 0590

1. INTRODUCTION

The Maxwell distribution of momentum (velocity) of molecules of an ideal gas in equilibrium is a well working and experimentally verified formula of kinetic theory. A recent paper ([1]) asserts that "It is impossible to consider a perfect gas of point molecules obeying special relativity. In such a gas the molecules do not interact, except with the walls of the container. In the approximation where the container is a rigid cube, the momentum component which is orthogonal to the wall changes sign. So does the corresponding speed component. The independence of the x, y, z components provides us with Maxwell-type distribution laws, laws of the exponential form $\exp[-\alpha(v_x^2 + v_y^2 + v_z^2)]$ and $\exp[-\beta(p_x^2 + p_y^2 + p_z^2)]$. These expressions are incompatible if $\mathbf{p} \neq m\mathbf{v}$."

On the contrary, there are treatments of relativistic kinetic theory and the Jüttner distribution – the relativistic counterpart of the Maxwell distribution – for the momentum of gas molecules is well known ([2],[3],[4]) and recently some papers generalize that distribution for the case when the mass of particles is a random variable ([5],[6]).

Nevertheless, it is worth examining the role of independence and the relation between the non-relativistic and relativistic results; for this purpose let us recall the deductions of the distributions.

There are three methods of obtaining the Maxwell distribution.

1. Maxwell ([7]) deduced his distribution from two elementary assumptions: 1) the distribution does not depend on the direction of velocity 2) the Cartesian components of velocity are independent. This simple deduction can be found in most of the textbooks on kinetic theory and it is known generally ([9],[10]).

2. Later Maxwell ([8],[11]) proved that his distribution is the only one for which the collision integral is zero, thus the Maxwell distribution can be deduced as the equilibrium solution of the Boltzmann equation.

3. According to Boltzmann's H-theorem, an equilibrium solution f of the Boltzmann equation maximizes the entropy $-k \int f(\mathbf{p}) \log(\mathbf{p}) d\mathbf{p}$; then the Maxwell distribution is deduced as the distribution which maximizes the entropy, provided the expectation of energy (and momentum) is fixed ([9]).

Maxwell himself felt that the assumption of independence in his first deduction is questionable. The other deductions do not use independence but according to the result – to the Maxwell distribution – the momentum (velocity) components are independent.

The momentum components and the velocity components are not independent in the Jüttner distribution.

Jüttner found his distribution by the third method, applied to the relativistic case ([2],[3]). The same result comes from the second method, too, applied to the relativistic case ([4]). Of course, the application of the first method cannot lead to the Jüttner distribution.

Let us return to the non-relativistic case. Since an equilibrium distribution (which is time independent and homogeneous in space) is looked for, in all the three methods – explicitly or implicitly – it is supposed that the gas is put into a container with *rigid* walls (the volume is constant).

All the three methods yield a distribution of the form $\exp\{-\beta \frac{|\mathbf{p}|^2}{2m}\}$ and the

physical meaning of β is not specified by the methods. To determine β , Maxwell followed Clausius' argument: the gas is in a container with *rigid and elastic* walls, and there is no interaction besides collision. The elastic collision of the molecules with the walls yield the pressure which, together with the state equation of ideal gases, result in $\beta = \frac{1}{kT}$.

It is an important fact, however, that *rigid and elastic walls contradict the Maxwell distribution*: if the walls are rigid and elastic then the energy of the gas is constant, consequently the energy of a molecule cannot be larger than this constant value; on the contrary, according to the Maxwell distribution, the energy of a molecule can be arbitrarily large with non-zero probability: *the momentum distribution of molecules of a gas in a container with rigid and elastic walls cannot be Maxwellian*.

In other words, if the momentum distribution of molecules is Maxwellian then the gas cannot be in a container with rigid and elastic walls i.e. the gas cannot be adiabatically insulated.

The Maxwell distribution seems to be compatible with a container having rigid and diathermic walls in a heat bath. Then the walls are "elastic in the mean" i.e. energy is not conserved in each collision but the average of energy in (a large number of) collisions is conserved. It is not hard to see that Clausius' argument can be applied in this case, too, and $\beta = \frac{1}{kT}$ can be derived.

Nevertheless, the question remains: *what is the distribution of momentum (velocity) if the walls are rigid and elastic (the gas has constant volume and is adiabatically insulated)?*

In this paper we approach the problem on the base of the theory of Gibbs ensembles, both non-relativistically and relativistically. A strictly constant energy of the gas (adiabatic insulation) corresponds to a microcanonical ensemble; a fixed average energy of the gas (heat bath) corresponds to a canonical ensemble.

2. MATHEMATICAL TOOLS

1. First of all we recall a usual notation: if U and V are sets and $f : U \rightarrow V$ is a function and G is a subset of V then

$$f^{-1}(G) := \{u \in U \mid f(u) \in G\}.$$

2. In statistical physics the phase space of one particle is called the μ -space and the phase space of a system of N particles is called the Γ -space; in other words, μ -space is \mathbb{R}^6 and Γ -space is $(\mathbb{R}^6)^N$.

Having these in mind we shall consider $\mathbf{X} := \mathbb{R}^d$ and \mathbf{X}^N where d is a positive integer. Subsets of \mathbf{X} and \mathbf{X}^N will always mean Borel subsets; they represent the events of a particle and a system of particles, respectively. A probability law P on \mathbf{X} will be called a *distribution* and a probability law L on \mathbf{X}^N will be called an *ensemble*.

We assume that the particles are indistinguishable; this will be reflected in the fact that the ensembles are invariant under permutations of particles. More precisely, if π is a permutation of $\{1, \dots, N\}$ then we put $R_\pi(\mathbf{x}_1, \dots, \mathbf{x}_N) := (\mathbf{x}_{\pi(1)}, \dots, \mathbf{x}_{\pi(N)})$ for $(\mathbf{x}_1, \dots, \mathbf{x}_N)$ in \mathbf{X}^N and we require that every ensemble L satisfy $L \circ R_\pi^{-1} = L$.

The i -th canonical projection is the map $\text{pr}_i : \mathbf{X}^N \rightarrow \mathbf{X}$, $(\mathbf{x}_1, \dots, \mathbf{x}_N) \mapsto \mathbf{x}_i$ ($i = 1, \dots, N$). If A is a subset of \mathbf{X} then $L(\text{pr}_i^{-1}(A))$ is the probability that the event A happens to the i -th particle in the ensemble L . In other words, $L \circ \text{pr}_i^{-1}$ is a distribution; because of the permutation invariance, this is the same distribution for all i , called the *distribution determined by the ensemble* and is denoted by P_L . Thus $P_L(A)$ is the probability that the event A happens to an arbitrarily chosen particle.

We say that an ensemble L has a density function if there is a $\varphi : \mathbf{X}^N \rightarrow \mathbb{R}$ such that

$$L(B) = \int_B \varphi(\mathbf{x}_1, \dots, \mathbf{x}_N) d\mathbf{x}_1, \dots, d\mathbf{x}_N$$

for all subsets B of \mathbf{X}^N (note that \mathbf{x}_k denotes d variables for all k).

It is defined similarly, according to the sense, that a distribution has a density function.

If the ensemble L has a distribution function φ then the distribution P_L has the density function

$$\mathbf{x} \mapsto \rho(\mathbf{x}) := \int \varphi(\mathbf{x}, \mathbf{x}_2, \dots, \mathbf{x}_N) d\mathbf{x}_2 \dots d\mathbf{x}_N.$$

It may happen that the ensemble L has no density function but P_L does have.

3. The Hamiltonian is a continuously differentiable function $H : \mathbf{X}^N \rightarrow \mathbb{R}$ whose derivative DH (the vector consisting of the partial derivative of H) is nowhere zero.

The canonical ensemble corresponding to the Hamiltonian H and to the fixed temperature T is given by the density function

$$C_{N,T} \exp\left(-\frac{H}{kT}\right)$$

where $C_{N,T}$ is a constant.

The microcanonical ensemble corresponding to the Hamiltonian H and to the fixed energy value E is concentrated onto the surface $S := H^{-1}\{E\}$ and is uniformly spread with respect to the surface measure σ of S , divided by the modul of the derivative of H ; in symbols, it is

$$C_{N,E} \frac{\sigma}{|DH|}$$

where $C_{N,E}$ is a constant.

4. We recall that if a surface S in \mathbb{R}^n is the graph of a function $u : \mathbb{R}^{n-1} \rightarrow \mathbb{R}$ (i.e. $S = \{x, u(x)\}$) then the surface measure is given by

$$\sqrt{1 + |Du(x_1, \dots, x_{n-1})|^2} dx_1 \dots dx_{n-1}.$$

Suppose now that $S = H^{-1}\{E\}$. Then the equality $H(x_1, \dots, x_n) = E$ allows us to express, at least locally, a variable as a function of the other $n - 1$ variables; without loss of generality, we take the n -th variable:

$$x_n = u(x_1, \dots, x_{n-1}).$$

Then (a part of) S is parametrized by the variables x_1, \dots, x_{n-1} i.e. it becomes the graph of u . Moreover, we have

$$\frac{\partial u}{\partial x_k} = -\frac{\frac{\partial H}{\partial x_k}}{\frac{\partial H}{\partial x_n}} \quad (k = 1, \dots, n-1).$$

Consequently, in this parametrization, $\frac{\sigma}{|DH|}$ becomes

$$\frac{1}{\left|\frac{\partial H}{\partial x_n}\right|} dx_1 \dots dx_{n-1}.$$

5. We shall consider an ideal gas consisting of N identical particles with mass m in a container with rigid walls. This means that there is no potential energy, the Hamiltonian does not depend on position, consequently the spatial part of the ensembles and distributions is trivial, so it is out of interest; we shall concentrate on the momentum part i.e. we take $\mathbf{X} := (\mathbb{R}^3)^N$ (N copies of the momentum space). The Hamiltonian has the form

$$H(\mathbf{p}_1, \dots, \mathbf{p}_N) = \sum_{i=1}^N h(\mathbf{p}_i)$$

where h is the kinetic energy of a particle,

$$h(\mathbf{p}) = \begin{cases} \frac{|\mathbf{p}|^2}{2m} & \text{non-relativistically,} \\ c\sqrt{|\mathbf{p}|^2 + m^2c^2} - mc^2 & \text{relativistically} \end{cases}$$

where c is the light speed.

3. IDEAL GAS IN A CONTAINER WITH RIGID AND DIATHERMIC WALLS IN A HEAT BATH

In this case the gas corresponds to a canonical ensemble, whose distribution function, both non-relativistically and relativistically, is

$$C_T^N \exp\left(-\frac{H(\mathbf{p}_1, \dots, \mathbf{p}_N)}{kT}\right) = \prod_{i=1}^N C_T \exp\left(-\frac{h(\mathbf{p}_i)}{kT}\right)$$

where T is the temperature of the heat bath. The distribution determined by this ensemble is

$$C_T \exp\left(-\frac{h(\mathbf{p})}{kT}\right)$$

which is the Maxwell distribution in the non-relativistic case and the Jüttner distribution in the relativistic case.

4. IDEAL GAS IN A CONTAINER WITH RIGID AND ELASTIC (ADIABATIC) WALLS

4.1. Dependence of components of momentum.

First of all we show that momentum (velocity) components cannot be independent in this case. Let E denote the constant total kinetic energy of the gas. Then the momentum $\mathbf{p} = (p_1, p_2, p_3)$ of a particle can vary in the set

$$B_E := \{h(\mathbf{p}) \leq E\} = \begin{cases} \{|\mathbf{p}|^2 \leq 2mE\} \\ \{|\mathbf{p}|^2 \leq 2mE + E^2/c^2\}; \end{cases}$$

here and in the following the upper and the lower lines refer to the non-relativistic and relativistic case, respectively.

We accept that B_E is the support of the distribution P of momentum values which means roughly that the momentum values outside of B_E have zero probability and every momentum value in B_E occurs with non-zero probability; more precisely, if G is an open subset then $P(G) = 0$ if G is disjoint from B_E and $P(G) \neq 0$ if G is not disjoint from B_E .

For $l = 1, 2, 3$ let G_l denote the set of momentum values (p_1, p_2, p_3) for which $\frac{2mE}{\sqrt{3}} < p_l$ holds in the non-relativistic case and the corresponding inequality is required in the relativistic case.

Note that

- G_l -s are open,
- G_l -s are not disjoint from B_E ,
- $\bigcap_{l=1}^3 G_l$ is disjoint from B_E .

Consequently, $P(G_l) \neq 0$ for all $l = 1, 2, 3$ and $P\left(\bigcap_{l=1}^3 G_l\right) = 0$.

Suppose the momentum components are independent under the probability law P ; then

$$\prod_{i=1}^3 P(G_i) = P\left(\bigcap_{l=1}^3 G_l\right)$$

which implies that one of $P(G_l)$ -s is zero; this contradiction proves that the momentum components cannot be independent.

Then it is trivial that the velocity components are also dependent in the non-relativistic case for velocity is proportional to momentum.

Velocity components are dependent in the relativistic case, too, since we can copy the above proof: the support of the probability law for velocity \mathbf{v} is $\{|\mathbf{v}| \leq c\}$.

4.2. General aspects of the distribution.

Since the total energy E of the gas is constant, the gas corresponds to a micro-canonical ensemble.

We have that

$$S := \overset{-1}{H}\{E\} = \begin{cases} \left\{ (\mathbf{p}_1, \dots, \mathbf{p}_N) \mid \sum_{i=1}^N \frac{|\mathbf{p}_i|^2}{2m} = E \right\} \\ \left\{ (\mathbf{p}_1, \dots, \mathbf{p}_N) \mid \sum_{i=1}^N c\sqrt{|\mathbf{p}_i|^2 + m^2 c^2} - Nmc^2 = E \right\}; \end{cases}$$

Enumerating the momentum components from 1 to $3N$ (i.e taking the identification $(\mathbb{R}^3)^N = \mathbb{R}^{3N}$ by $(\mathbf{p}_i)_l =: p_{3(i-1)+l}$, $i = 1, \dots, N$, $l = 1, 2, 3$), we split S into

three disjoint subsets S_+, S_0 and S_- , consisting of the elements for which p_{3N} is positive, zero and negative, respectively. S_0 has zero measure, and we can express p_{3N} as a function of the other components both on S_+ and S_- :

$$p_{3N} = u_{\pm}(p_1, \dots, p_{3N-1}) = \begin{cases} \pm \sqrt{2mE - \sum_{k=1}^{3N-1} p_k^2} \\ \pm \sqrt{\left(\frac{E+mc^2 - \sum_{i=1}^{N-1} h(\mathbf{p}_i)}{c}\right)^2 - p_{3N-2}^2 - p_{3N-1}^2 - m^2 c^2} ; \end{cases}$$

of course, the functions u_{\pm} are defined on the subset where the expression under the square root is positive.

In other words, S_+ and S_- are represented as the graph of the functions u_+ and u_- , respectively. Then, according to the formulae in Section 2, the probability of the event B of the gas (B is a subset of \mathbb{R}^{3N}) under the microcanonical ensemble in question is

$$C_{N,E} \sum_{+,-} \int_{u_{\pm}^{-1}(B \cap S_{\pm})} \frac{1}{\left| \frac{\partial H}{\partial p_{3N}} \right|_{\pm}} dp_1 \dots dp_{3N-1}$$

where

$$\begin{aligned} \left| \frac{\partial H}{\partial p_{3N}} \right|_{\pm} &:= \left| \frac{\partial H}{\partial p_{3N}}(p_1, \dots, p_{3N-1}, u_{\pm}(p_1, \dots, p_{3N-1})) \right| \\ &= \begin{cases} \frac{\sqrt{2mE - \sum_{k=1}^{3N-1} p_k^2}}{m} \\ c^2 \sqrt{\frac{\left(\frac{E+mc^2 - \sum_{i=1}^{N-1} h(\mathbf{p}_i)}{c}\right)^2 - p_{3N-2}^2 - p_{3N-1}^2 - m^2 c^2}{E+mc^2 - \sum_{i=1}^{N-1} h(\mathbf{p}_i)}} \end{cases} \end{aligned} \quad (1)$$

According to the definition of the distribution determined by the ensemble in question, the probability of the event A of a particle (A is a subset of \mathbb{R}^3) under the distribution is the probability of $\text{pr}_i^{-1}(A)$ under the ensemble where i is an arbitrary number between 1 and N . Here in the general considerations and in the non-relativistic case we take $i = 1$ whereas in the relativistic case we find convenient to choose $i = N - 1$.

For $\mathbf{p} = (p_1, p_2, p_3) \in B_E$, let us introduce the notation

$$V_{\mathbf{p}} := \{(p_4, \dots, p_{3N-1}) \mid (p_1, \dots, p_{3N-1}) \text{ is in the domain of } u_{\pm}\}.$$

Then we have that the probability of A is zero if A is disjoint from B_E and it is

$$C_{N,E} \int_A \sum_{+,-} \int_{V_{\mathbf{p}}} \frac{1}{\left| \frac{\partial H}{\partial p_{3N}} \right|_{\pm}} (dp_1 dp_2 dp_3) dp_4 \dots dp_{3N-1}$$

if A is contained in B_E .

Since $\left| \frac{\partial H}{\partial p_{3N}} \right|_+ = \left| \frac{\partial H}{\partial p_{3N}} \right|_-$, we obtain that the distribution has the density function

$$D_{N,E}(\mathbf{p}) = \begin{cases} \frac{K_{N,E}(\mathbf{p})}{\int_{B_E} K_{N,E}(\mathbf{p}') d\mathbf{p}'} & \text{if } h(\mathbf{p}) \leq E, \\ 0 & \text{if } h(\mathbf{p}) > E \end{cases} \quad (2)$$

where

$$K_{N,E}(\mathbf{p}) := \int_{V_{\mathbf{p}}} \frac{1}{\left| \frac{\partial H}{\partial p_{3N}} \right|_+} dp_4 \dots dp_{3N-1}. \quad (3)$$

4.3. The non-relativistic case.

4.3.1. The distribution.

Writing $2mE - \sum_{k=1}^{3N-1} p_k^2 = (2mE - |\mathbf{p}|^2) - \sum_{k=4}^{3N-1} p_k^2$ and applying polar coordinates in \mathbb{R}^{3N-4} , in view of (1) we have for the function defined in (3) that

$$K_{N,E}(\mathbf{p}) = a \int_0^{\sqrt{2mE - |\mathbf{p}|^2}} \frac{1}{\sqrt{2mE - |\mathbf{p}|^2 - r^2}} r^{3N-5} dr = b (2mE - |\mathbf{p}|^2)^{\frac{3N-5}{2}}$$

where a and b are constants.

Applying polar coordinates in \mathbb{R}^3 , a convenient substitution and the formula ([12])

$$\int_0^1 x^\alpha (1-x)^\beta dx = \frac{\Gamma(\alpha+1)\Gamma(\beta+1)}{\Gamma(\alpha+\beta+2)},$$

we can calculate the integral of $(2mE - |\mathbf{p}|^2)^{\frac{3N-5}{2}}$ with respect to \mathbf{p} and as a final result we have according to (2) that *the distribution of momentum of particles of a non-relativistic ideal gas in a container with rigid and elastic walls has the following density function:*

$$D_{N,E}(\mathbf{p}) = \begin{cases} \frac{\Gamma(\frac{3N}{2})}{\Gamma(\frac{3N-3}{2}) \pi^{3/2} (2mE)^{3/2}} \left(1 - \frac{|\mathbf{p}|^2}{2mE}\right)^{\frac{3N-5}{2}} & \text{if } |\mathbf{p}|^2 \leq 2mE, \\ 0 & \text{if } |\mathbf{p}|^2 > 2mE. \end{cases} \quad (4)$$

This is a distribution different from the Maxwellian one; Figures 1 and 2 compare them for neon molecules at a normal temperature, in the cases $N = 10$ and $N = 100$, respectively ($m = 3, 36 \cdot 10^{-26} kg$, $T = 300K$, $E = \frac{3}{2}kTN$); the fat lines draw the Maxwell distribution, the thin lines draw our distribution. The difference between the two distributions cannot be observed in this scale if $N \geq 1000$.

We see that though the analytic forms of the two distributions are different, their graphs are similar even for few molecules and they coincide practically for a large number of molecules. This is confirmed by the following result.

4.3.2. The thermodynamic limit.

It is a routine to calculate the expectation of the energy of a particle under the distribution (4):

$$\frac{\Gamma(\frac{3N}{2})}{\Gamma(\frac{3N-3}{2}) \pi^{3/2} (2mE)^{3/2}} \int_{|\mathbf{p}|^2 \leq 2mE} \frac{|\mathbf{p}|^2}{2m} \left(1 - \frac{|\mathbf{p}|^2}{2mE}\right)^{\frac{3N-5}{2}} d\mathbf{p} = \frac{E}{N}.$$

Let us increase the number of particles of the gas in such a way that the expectation of the energy of a particle – in other words, the specific energy E/N – is constant. Putting

$$\frac{E}{N} =: \frac{3}{2}kT.$$

we obtain that

$$D_{N,(3N/2)kT}(\mathbf{p}) = \left(\frac{\Gamma\left(\frac{3N}{2}\right)}{\Gamma\left(\frac{3N-3}{2}\right)\Gamma\left(\frac{3N}{2}\right)} \right) \left(\frac{m}{2\pi kT} \right)^{3/2} \left(1 - \frac{|\mathbf{p}|^2}{2mkT} \frac{1}{3N/2} \right)^{\frac{3N-5}{2}}$$

if $|\mathbf{p}|^2 \leq (3mkT)N$.

Then Stirling's formula ([12])

$$\Gamma(\alpha + 1) = \alpha^{\alpha+1/2} e^{-\alpha} \sqrt{2\pi} \left(1 + \text{Ordo} \left(\frac{1}{\alpha} \right) \right)$$

and the well known limit procedure of obtaining the powers of e yield that our distribution tends to the Maxwellian one:

$$\lim_{N \rightarrow \infty} D_{N,(3N/2)kT}(\mathbf{p}) = \left(\frac{m}{2\pi kT} \right)^{3/2} e^{-\frac{|\mathbf{p}|^2}{2mkT}}.$$

It is worth mentioning that the convergence is uniform.

4.4. The relativistic case.

4.4.1. An integral form of the distribution.

Now we choose the $(N - 1)$ -th particle to determine the distribution from the microcanonical ensemble. According to (1), the function defined in (3) is of the form

$$K_{N,E}(\mathbf{p}) = \int_{V_{\mathbf{p}}} \frac{\left(E + mc^2 - \sum_{i=1}^{N-1} h(\mathbf{p}_i) \right) d\mathbf{p}_1 \dots d\mathbf{p}_{N-2} dp_{3N-2} dp_{3N-1}}{c^2 \sqrt{\left(\frac{E + mc^2 - \sum_{i=1}^{N-1} h(\mathbf{p}_i)}{c} \right)^2 - p_{3N-2}^2 - p_{3N-1}^2 - m^2 c^2}}$$

where $\mathbf{p} := \mathbf{p}_{N-1}$; take care that $N - 1$ vector variables $\mathbf{p}_1, \dots, \mathbf{p}_{N-1}$ and two scalar variables p_{3N-2}, p_{3N-1} are involved in this formula.

The integration with respect to the two scalar variables can be calculated by the use of polar coordinates; the integration extends over the region described by the inequality

$$p_{3N-2}^2 + p_{3N-1}^2 < \left(\frac{E + mc^2 - \sum_{i=1}^{N-1} h(\mathbf{p}_i)}{c} \right)^2 - m^2 c^2.$$

With the notation

$$F_{N,E}(\mathbf{p}_1, \dots, \mathbf{p}_{N-1}) := \frac{E + mc^2 - \sum_{i=1}^{N-1} h(\mathbf{p}_i)}{c^2} \sqrt{\left(\frac{E + mc^2 - \sum_{i=1}^{N-1} h(\mathbf{p}_i)}{c}\right)^2 - m^2 c^2} \quad (5)$$

(the domain of F consists of the momentum values for which the expression under the square root is positive), we obtain

$$K_{N,E}(\mathbf{p}) = 2\pi \int F_{N,E}(\mathbf{p}_1, \mathbf{p}_2, \dots, \mathbf{p}_{N-2}, \mathbf{p}) d\mathbf{p}_1 \dots d\mathbf{p}_{N-2} \quad (6)$$

where the integration extends over the region

$$\left\{ (\mathbf{p}_1, \dots, \mathbf{p}_{N-2}) \mid \sum_{i=1}^{N-2} h(\mathbf{p}_i) < E - h(\mathbf{p}) \right\}.$$

The density function $D_{N,E}$ of the momentum distribution of particles of a relativistic ideal gas in a container with rigid and elastic walls is obtained from (5) and (6) by the formula (2).

If $m \neq 0$ then we cannot give this density function in an explicit form. It is not hard to see that the non-relativistic limit (when c tends to infinity) of this density function equals the one given in (4).

4.4.2. The distribution for the photon gas.

If $m = 0$ then we can calculate the above integrals easily. Namely, in this case

$$K_{N,E}(\mathbf{p}) = \frac{2\pi}{c} \int \left(\frac{E}{c} - |\mathbf{p}| - \sum_{i=1}^{N-2} |\mathbf{p}_i| \right)^2 d\mathbf{p}_1 \dots d\mathbf{p}_{N-2};$$

the integration extends over the region where the expression between parantheses is positive. Applying the substitution $\mathbf{p}_i := \left(\frac{E}{c} - |\mathbf{p}|\right) \mathbf{z}_i$ ($i = 1, \dots, N - 2$), we obtain that

$$K_{N,E}(\mathbf{p}) = \text{const.} \left(\frac{E}{c} - |\mathbf{p}| \right)^{3N-4}.$$

Using polar coordinates in \mathbb{R}^3 , we find that

$$\begin{aligned} \int_{|\mathbf{p}| < E/c} \left(\frac{E}{c} - |\mathbf{p}| \right)^{3N-4} d\mathbf{p} &= 4\pi \int_0^{E/c} \left(\frac{E}{c} - r \right)^{3N-4} r^2 dr = \\ &= 4\pi (E/c)^{3N-1} \frac{\Gamma(3N-3)\Gamma(3)}{\Gamma(3N)}. \end{aligned}$$

Consequently, for $m = 0$, we have the explicit form

$$D_{N,E}(\mathbf{p}) = \frac{1}{8\pi} \left(\frac{3Nc}{E} \right)^3 \left(1 - \frac{3}{3N} \right) \left(1 - \frac{2}{3N} \right) \left(1 - \frac{1}{3N} \right) \left(1 - \frac{c|\mathbf{p}|}{E} \right)^{3N-4}. \quad (7)$$

4.4.3. The thermodynamic limit.

As in the non-relativistic case, we easily find that the expectation of the energy of a photon is E/N . Then putting

$$3kT := \frac{E}{N},$$

keeping this quantity constant and letting N tend to infinity in (7), we obtain as a uniform limit the well known usual density function of the photon gas ([3]):

$$\lim_{N \rightarrow \infty} D_{N,3NkT}(\mathbf{p}) = \frac{1}{8\pi} \left(\frac{c}{kT} \right)^3 \exp \left(-\frac{c|\mathbf{p}|}{kT} \right).$$

Though the density function for $m \neq 0$ is not given explicitly by elementary functions, we can determine its thermodynamic limit as follows.

We let the number of particles increase in such a way that the specific energy is constant i.e. we put $E = Ne$ where e is a fixed nonnegative constant. For the sake of simplicity, now the functions defined in (5), (6) and the density function will be labelled by a single subscript referring to the number of particles: K_N , F_N and D_N . Moreover, we note that all these functions depend on momenta through the hamiltonians:

$$K_N(\mathbf{p}) = 2\pi\kappa_N(h(\mathbf{p})), \quad D_N(\mathbf{p}) = \Delta_N(h(\mathbf{p})), \quad (8)$$

$$F_N(\mathbf{p}_1, \dots, \mathbf{p}_{N-1}) = \Phi_N(h(\mathbf{p}_1), \dots, h(\mathbf{p}_{N-1}))$$

where

$$\Phi_N(x_1, \dots, x_{N-1}) := \frac{Ne + mc^2 - \sum_{i=1}^{N-1} x_i}{c^2} \sqrt{\left(\frac{Ne + mc^2 - \sum_{i=1}^{N-1} x_i}{c} \right)^2 - m^2 c^2}$$

is defined for nonnegative real numbers x_1, \dots, x_{N-1} which satisfy $\sum_{i=1}^{N-1} x_i < Ne$.

It is obvious that

$$\Phi_{N-1}(x_1, \dots, x_{N-2} + x_{N-1} - e) = \Phi_N(x_1, \dots, x_{N-1}) = \Phi_{N+1}(x_1, \dots, x_{N-1}, e).$$

As a consequence, according to (6), we have for $h(\mathbf{p}) < Ne$

$$\begin{aligned} \kappa_N(h(\mathbf{p})) &= \int_{\sum_{i=1}^{N-2} h(\mathbf{p}_i) < Ne - h(\mathbf{p})} \Phi_N(h(\mathbf{p}_1), \dots, h(\mathbf{p}_{N-2}), h(\mathbf{p})) d\mathbf{p}_1 \dots d\mathbf{p}_{N-2} \\ &= \int \left(\int \Phi_{N-1}(h(\mathbf{p}_1), \dots, h(\mathbf{p}_{N-2}) + h(\mathbf{p}) - e) d\mathbf{p}_1 \dots d\mathbf{p}_{N-3} \right) d\mathbf{p}_{N-2} \\ &= \int_{h(\mathbf{p}') < Ne - h(\mathbf{p})} \Theta_{N-1}(h(\mathbf{p}') + h(\mathbf{p}) - e) d\mathbf{p}' \end{aligned}$$

and

$$\begin{aligned}
\int_{h(\mathbf{p}) < Ne} \Theta_N(h(\mathbf{p})) d\mathbf{p} &= \int \Phi_N(h(\mathbf{p}_1), \dots, h(\mathbf{p}_{N-2}), h(\mathbf{p}_{N-1})) d\mathbf{p}_1 \dots d\mathbf{p}_{N-2} d\mathbf{p}_{N-1} \\
&= \int_{\sum_{i=1}^{N-1} h(\mathbf{p}_i) < Ne} \Phi_{N+1}(h(\mathbf{p}_1), \dots, h(\mathbf{p}_{N-1}), e) d\mathbf{p}_1 \dots d\mathbf{p}_{N-1} \\
&= \Theta_{N+1}(e).
\end{aligned}$$

Thus from (2) and (8) we get the following iteration (with $x := h(\mathbf{p}) < Ne$):

$$\begin{aligned}
\Delta_N(x) &= \frac{\Theta_N(x)}{\Theta_{N+1}(e)} = \frac{\Theta_N(e)}{\Theta_{N+1}(e)} \frac{\int \Theta_{N-1}(h(\mathbf{p}') + x - e) d\mathbf{p}'}{\Theta_N(e)} \\
&= \Delta_N(e) \int_{h(\mathbf{p}') < Ne} \Delta_{N-1}(h(\mathbf{p}') + x - e) d\mathbf{p}'
\end{aligned}$$

for the distribution.

Letting N tend to infinity and supposing that the sequence of density functions is uniformly convergent as in the previous two cases, we get the following integral equation for the limit distribution (which will be continuous)

$$\Delta(x) = \Delta(e) \int \Delta(h(\mathbf{p}') + x - e) d\mathbf{p}' \quad (0 \leq x, 0 < e)$$

where the integration extends over all momentum space. Then

$$\Delta(x + e) = \Delta(e) \int \Delta(h(\mathbf{p}') + x) d\mathbf{p}'$$

and taking the limit $e \rightarrow 0$, we get

$$\Delta(x) = \Delta(0) \int \Delta(h(\mathbf{p}') + x) d\mathbf{p}'$$

from which we conclude that

$$\Delta(0)\Delta(x + e) = \Delta(x)\Delta(e) \quad (0 \leq x, 0 \leq e).$$

Since Δ is continuous, it follows that

$$\Delta(x) = C \exp(-\beta x)$$

where C and β are positive constants (the positivity of β is assured by the integrability of $\mathbf{p} \mapsto \Delta(h(\mathbf{p}))$).

Thus accepting that $\beta = \frac{1}{kT}$, we obtained that the thermodynamic limit of our distribution is the Jüttner distribution:

$$\lim_{N \rightarrow \infty} D_N(\mathbf{p}) = \Delta(h(\mathbf{p})) = C \exp\left(-\frac{c\sqrt{\mathbf{p}^2 + m^2 c^2} - mc^2}{kT}\right).$$

5. DISCUSSION

The Maxwell distribution and the Jüttner distribution correspond to an ideal gas in a container with *rigid* and *diathermic* walls in a heat bath. In this paper we have given the distribution of momentum for a gas in a container with *rigid* and *adiabatic (elastic)* walls, both non-relativistically and relativistically. The non-relativistic density function of the distribution is given explicitly by the formula (4); the relativistic density function is presented in an implicit form by the expressions (5), (6) and (2) which result in the explicit function (7) in the case of zero mass (photon gas). The thermodynamic limit of our distributions gives back the usual ones.

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