PHYSNET

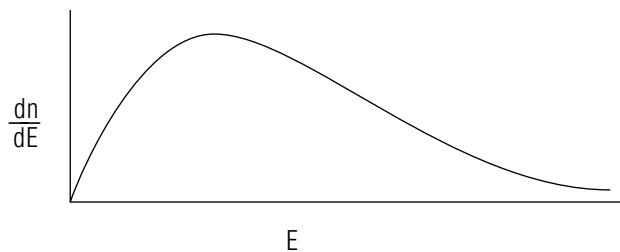# ENERGY AND BOLTZMANN DISTRIBUTIONS

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ENERGY AND BOLTZMANN DISTRIBUTIONS
by
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Michigan State University

Title: **Energy and Boltzmann Distributions**

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Length: 1 hr; 20 pages

Input Skills:

1. Describe an ideal gas in terms of (a) the relationship between temperature and the speed of its molecules and (b) the nature of the interactions among its molecules. (MISN-0-157)

Output Skills (Knowledge):

K1. Define the partition of a system consisting of N molecules of a gas.

K2. Define thermal equilibrium starting from the concept of a very large number of possible partitions for a given many particle system. Identify the partition for an ideal gas in thermal equilibrium.

Output Skills (Problem Solving):

S1. Determine the number of particles that have their energies in a given energy range, given the partition for the many particle system.

S2. Given the partition, calculate the average values of kinetic energy, speed and speed squared and the total energy of a system of N molecules of a gas.

External Resources (Required):

1. K. W. Ford, *Classical and Modern Physics*, Vol. 2, Xerox (1972). For availability, see this module's *Local Guide*.

2. M. Alonso and E. J. Finn, *Physics*, Addison-Wesley (1970). For availability, see this module's *Local Guide*.

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New authors, reviewers and field testers are welcome.

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1. Introduction

In a gas in thermal equilibrium at a given temperature T, the average kinetic energy of the molecules of that gas has a definite value. For an ideal gas, in fact, the linear relationship $E_{K,ave} = (3/2)kT$ defines the temperature of that gas. However, the energy of an individual molecule of that gas varies from instant to instant, changing from collision to collision and at any one instant the individual energies of the molecules are distributed over a broad range of values about the average energy. As a consequence of the very large number of molecules in a gas sample ($\geq 10^{20}$ molecules), the probability that any one molecule will have any given energy value can be known to very high precision when the gas is in thermal equilibrium. This probability distribution gives us the distribution of particles among the possible energy values and is given by the Boltzmann distribution function for an ideal gas in thermal equilibrium. In this unit distribution functions in general and the Boltzmann function in particular will be introduced.[1]

2. Energy Distribution Functions

2a. General Distribution Functions. Suppose we have a system of N molecules and a set of L available energies such that any one of the N molecules could have any of the L energies. Then there are very many possible ways that the N molecules could have energies allocated to them. For example all of the molecules could have energy E_9, or maybe 1/5 of the molecules could have energy E_7 and the other 4/5 have energy E_{33}, or the energies could be all equally populated, meaning the molecules are divided up evenly among them, and so forth. The numbers that tell how many of the molecules have each of the energies is called the partition, or distribution; that is, if n_1 molecules have energy E_1, n_2 have energy E_2, and so on up to n_L molecules with energy E_L, then the set of numbers

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[1] A concept intimately related to the probability distribution of the particles of a gas amongst the possible energy states of the system is entropy. See "Entropy" (MISN-0-160).

n_1, n_2, ..., n_L is the partition. If one knows the partition, it is easy to calculate a system's total energy:

$$E_{total} = n_1 E_1 + n_2 E_2 + \ldots + n_L E_L = \sum_{i=1}^{L} n_i E_i \,,$$

and its average energy:

$$E_{ave} = \frac{E_{total}}{N} = \frac{\sum_{i=1}^{L} n_i E_i}{N} \,.$$

Notice that since N is the total number of molecules, we also know:

$$N = n_1 + n_2 + \ldots n_L = \sum_{i=1}^{L} n_i \,.$$

Many different distributions are possible, we said. However, a many-particle system *in thermal equilibrium* can be shown by both theory and experiment to have only one distribution, determined by the system's temperature.

2b. Thermal Equilibrium. At thermal equilibrium a system is in its most probable distribution and thus may also be said to be in statistical equilibrium. The more particles there are in a system, the more probable the most probable distribution is; the very large number of molecules in even a small quantity of gas makes the most probable distribution very stable and the fluctuations around it very small. The energy of any one molecule changes drastically and rapidly as it collides with other molecules in the system. Since, however, the molecules of an ideal gas collide elastically, one's loss is literally another's gain, and since there are so very many of them, for every molecule that attains energy E_i another loses energy E_i. At thermal equilibrium, the total number of molecules with any given energy is constant, even though the individual particles trade energies rapidly among themselves.

2c. The Boltzmann Distribution. The most probable distribution for an ideal gas is a well known function called the Boltzmann distribution (or the Maxwell-Boltzmann distribution). It can be derived by statistical mechanics and is given by:

$$\frac{dn}{dE} = \frac{2\pi N}{(\pi kT)^{3/2}} E^{1/2} e^{-E/kT}.$$

The general shape of this function is shown in Fig. 1. Notice now we have not written the distribution in the form of a set of numbers n corresponding to specific energies E but rather in the form of a continuous function that can tell us the number of molecules having energies within a range of energies. The reasons for this are discussed in Exercise B. The model for an ideal gas is a system of small round particles whose only energy is their kinetic energy. That means that their distribution function could be in terms of speed instead of energy simply by substituting $E = mv^2/2$ and $dE = mv\,dv$. Thus the speed distribution of an ideal gas is:

$$\frac{dn}{dv} = 4\pi N \left(\frac{m}{2\pi kT}\right)^{3/2} v^2 e^{-mv^2/2kT}.$$

The functions dn/dE and dn/dv plotted as functions of E and v, respectively, obviously do not have the same shape.[2] Nevertheless, they do have several characteristics in common: they are equal to zero at $E = 0$ or $v = 0$; both go to zero exponentially at high values of E or v; and both have a maximum at some most probable value of E or v, the position and shape of the peak depending on the temperature T. At low temperatures both dn/dE and dn/dv have high, narrow peaks near $E = 0$ or $v = 0$, corresponding to a system with most of its particles moving relatively slowly. At high temperatures, on the other hand, both functions have low, broad peaks at high values of E or v, corresponding to a system of particles moving both rapidly and with a relatively wide range of speeds.

3. Readings

For access to the following readings, see this module's *Local Guide*.

Read pages 609-619 of "Classical and Modern Physics," Vol. 2, by K. W. Ford.[3] This reading selection develops the connection between partition probability and equilibrium.

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[2]Notice in particular that near $E = 0$, dn/dE starts out like $y = \sqrt{x}$ whereas near $v = 0$, dn/dv starts out like $y = x^2$.

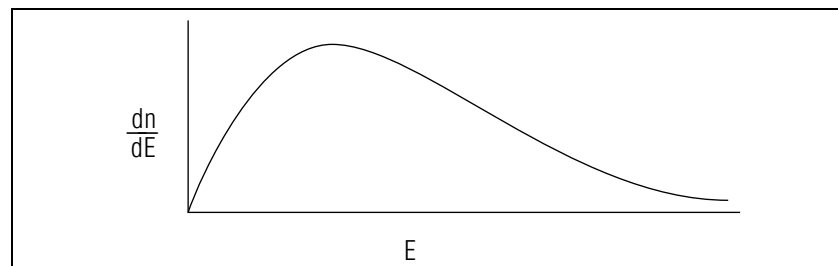[3]For availability, see this module's *Local Guide*.

Figure 1. The Maxwell-Boltzmann distribution.

Read Section 13.4 (p. 257) of "Physics" by M. Alonso and E.J. Finn.[4]

4. Exercises

A. Consider the following partition shown in the table below (n_i is the number of particles with energy E_i):

i	n_i	E_i (joules)
1	0.5×10^{18}	1.60×10^{-21}
2	1.0×10^{18}	2.40×10^{-21}
3	1.8×10^{18}	3.20×10^{-21}
4	1.2×10^{18}	4.00×10^{-21}
5	0.6×10^{18}	4.81×10^{-21}

with no other energies represented.

a. What are the average kinetic energy and the total internal energy for the particles of this system?

b. How many moles of substance are there in this gas?

c. Could this system, represented by this above partition, be in thermal equilibrium? Explain.

d. Can you assign a temperature to this gas with this partition? Explain.

e. When thermal equilibrium gets established, if this system is isolated so that none of the energy gets away, what can we say about the temperature? What about the energy partition?

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[4]For availability, see this module's *Local Guide*.

B. The partition described in Exercise A was a discrete partition. That is, 9.8% of the particles had energy equal to exactly 1.60×10^{-21} joules each, 19.6% of them had 2.40×10^{-21} joules each, 35.3% had 3.20×10^{-21} joules, 23.5% had 4.00×10^{-21} joules, and 11.8% had 4.81×10^{-21} joules. No other energies were represented. No particle, for example, had an energy anywhere in the range between 1.60×10^{-21} joules and 2.40×10^{-21} joules, although about 10^{18} of them had exactly either of these two energies.

In any physical situation, as a result of the many collisions that occur in such a many-particle system the energy distribution will quickly spread to "fill in the blank spaces" between the discrete n_i's so that there is a continuous distribution: you will find particles with any energy (within the limitations set by the total energy of the system. Later you'll see that Quantum Mechanics also imposes limitations. So how do you describe the energy partition in this case?

You cannot write down the partition in tabular form, as was done in Exercise A, unless your table includes every possible energy in some continuous range. Then you run into what may seem like a contradiction, because there are an infinite number of possible energies and only a finite number of particles the most likely partition from the discrete tabulation point of view is zero particles at any one specified energy. That is why it makes more sense, when a continuous range of energies is possible, to describe the partition with a *density function* (the number of particles per unit energy in the vicinity of specified energy value). The Maxwell-Boltzmann distribution function is such a density function. (It is the correct density function which gives the energy partition of an ideal gas after thermal equilibrium has been established.)

A prototype of a density function dn/dE is plotted vs E, the energy, in Fig. 2. Note that it can also be expressed and plotted as a function of v, the velocity.

What does a point on such a curve tell you? Or if dn/dE was given to you as a function of E and you evaluated it at a specific value of the energy, E_0 what would this number tell you? It would not tell you the number of particles that have energy E_0. For one thing, it has the dimensions of number per unit energy, not number. Also, we concluded above, the number of particles that have precisely the energy E_0 is zero for all values of E_0. From calculus, $(dn/dE)\,dE$ is dn, the infinitesimal
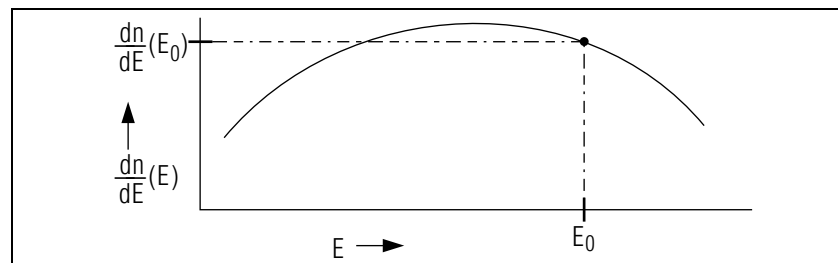
Figure 2. A prototypical number density (number per unit energy), plotted as a function of energy.

increment in the variable n. For finite (but small) increments, ΔE, then:

$$\frac{dn}{dE}\Delta E = \Delta n.$$

This has the interpretation of being the *finite increment* in n in the neighborhood where dn/dE is evaluated. In our case, n is the number of particles in an energy increment E around the point on the curve where dn/dE is evaluated.

Consider the curve depicted in Fig. 2. Suppose at energy $E = 2 \times 10^{-21}$ joules the value of the function dn/dE is $2 \times 10^{24}/$,J meaning 2×10^{24} particles per joule. How many particles are there in an energy range 0.002×10^{-21} J around this value of E_0? How many are there in a larger interval, $\Delta E = 0.02 \times 10^{-21}$ joules? or the interval $\Delta E = 0.2 \times 10^{-21}$ joules? The answers you got should have been 4, 40, and 400 particles, respectively. The first of these says that 4 particles in the system can be expected to have their energy between 1.999×10^{-21} joules and 2.001×10^{-21} joules, and in the last interval, there are 400 particles with individual energies somewhere between 1.9×10^{-21} joules and 2.1×10^{-21}
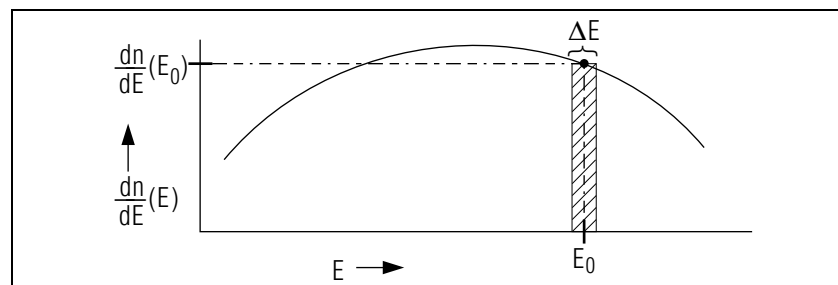

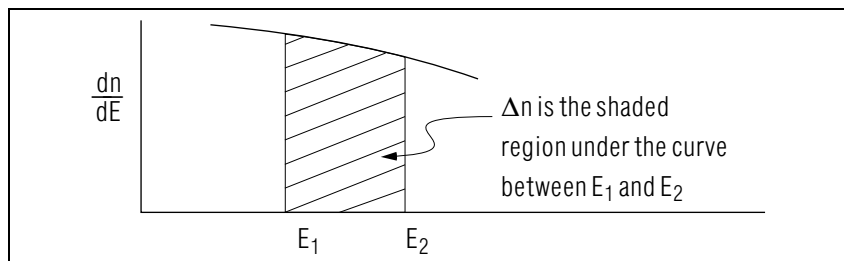**Figure 3.** As in Fig. 2, relating number density to numbers.

Figure 5. Relating rate-area to number.

joules.

Let's examine Fig. 3 more closely. The area of the shaded rectangle is just dn/dE times ΔE: dn/dE is the height, ΔE the width. Except for the deviations at the top of the rectangle, this is *almost* the area under the curve in the interval ΔE. (see Fig. 4)

The smaller ΔE is, the closer this is to the area under the curve. In the limit where ΔE goes to the infinitesimal dE, we can see that the number of particles in the interval between E_1 and E_2 is Δn. (see Fig. 5)

$$\int_{E_1}^{E_2} \frac{dn}{dE}\, dE = \Delta n.$$

Because of the reasons discussed above, we need to think from the point of view of continuous distributions rather than discrete ones.

With this lengthy prologue, examine the distribution illustrated in Fig. 6, where the number of particles per unit energy interval is zero for all energies except between E_1 and E_2, where it is a constant C. Consider the shaded rectangular energy region of width $\Delta E = E_b - E_a$.
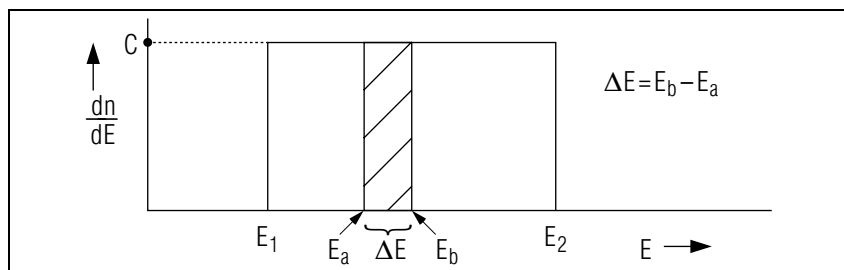

Figure 6. Number distribution for Problem B.

a. How many particles can be expected to have their energy between E_a and E_b?

b. If the total number of particles in the system is N, what is the value of C?

c. What is the total number of particles with their energy between E_b and infinity? (Express your answer in terms of N.)

d. Is this system in thermal equilibrium? Explain.

C.

a. Refer to the figure in Problem 4 of the *Problem Supplement* (dn/dE for a gas satisfying the Maxwell-Boltzmann distribution law). What is the total number of molecules in the gas? Give a qualitative answer here.

b. Again referring to the same figure, what is the expression (in integral form) that gives you the number of particles with energy greater than E_2? Compare the result of this integration at the two temperatures 300 K and 500 K.

D. The Boltzmann distribution is given by:

$$\frac{dn}{dE} = CE^{1/2}e^{-\beta E}, \qquad \beta = \frac{1}{kT},$$

where C and β are independent of energy. At very low E, the $E^{1/2}$ makes this function go to zero, while at high E the exponential forces it to zero, so there is a maximum somewhere between.

a. For what value of E does this maximum occur? The average value of some measurable quantity A is given by:

$$A_{ave} = \frac{A_1 + A_2 + \ldots + A_N}{N},$$

where each A_i is one of the measured values and there are N of them. This can also be written:

$$A_{ave} = \frac{n_1 A_1 + n_2 A_2 + \ldots + n_p A_p}{N},$$

where n_i is the number of times A_i is measured. If, as in the case of the energy of the particles in a gas, there is a continuous range of possible values of A, the discrete sum must go over to the integral:

$$A_{ave} = \frac{1}{N} \int A \frac{dn}{dA} \, dA.$$

Note that the factor on the right, $(dn/dA) \, dA$, is the number of particles that have their A value between A and $A + dA$.

Thus the average energy of a system of particles is given by:

$$E_{ave} = \frac{1}{N} \int_0^\infty E \frac{dn}{dE} \, dE.$$

$$E_{ave} = \frac{\int_0^\infty E \frac{dn}{dE} \, dE}{\int_0^\infty \frac{dn}{dE} \, dE},$$

the denominator being just N, the total number.

b. For the distribution given in Exercise B, what is the average energy?

c. For the Boltzmann distribution,

$$\frac{dn}{dE} = CE^{1/2}e^{-\beta E}, \ \beta = \frac{1}{kT},$$

find the value of C by using the condition that the total number of particles is N. You'll need to refer to a table of integrals. If you don't have one, use:

$$\int_0^\infty x^{n-1}e^{-x} \, dx = \Gamma(n),$$

where:

$$\Gamma(n+1) = n\Gamma(n) \quad \text{and} \quad \Gamma(1/2) = \sqrt{\pi}.$$

d. Evaluate the average energy for a system of particles that have their energies distributed cording to the Boltzmann distribution.

5. Answers to Exercises

A.

a. $U = 16.6 \times 10^{-3}$ joules, $E_{ave} = 3.26 \times 10^{-21}$ joules.

b. 8.5×10^{-6} moles

c. No. When the thermal equilibrium is established, the distribution of energy among the molecules is given by the Boltzmann distribution, which is the *most probable* partition of the many possible partitions.

d. No. Temperature is defined for systems in thermal equilibrium. However, in more advanced treatments of thermodynamics, systems not in thermal equilibrium may have temperatures defined for them. In fact, our above system by that definition then has a negative temperature!

e. This system, with $E_{ave} = 3.26 \times 10^{-21}$ joules, would have temperature $T = 157\,\text{K}$ if thermal equilibrium were established while E_{ave} remained unchanged. The energy partition would be given by the Boltzmann distribution whose $T = 157\,\text{K}$ and which has $N = 5.1 \times 10^{18}$ total number of particles.

B.

a. $C \, \Delta E$.

b. $C = \dfrac{N}{E_2 - E_1}$.

c. $n(E > E_b) = N \dfrac{E_2 - E_b}{E_2 - E_1}$.

d. No, for the same reason as in part (c) of Exercise A.

C.

a. The total area under the curve.

b. $\int_{E_2}^\infty \frac{dn}{dE} \, dE$. At $500\,\text{K}$ there are more particles with $E > E_2$.

D.

a. The most probable $E = KT/2$, the point on the curve where the maximum occurs.

b. $(E_2 + E_1)/2$.

c. $N = \int_0^\infty \frac{dn}{dE} \, dE = C \int_0^\infty E^{1/2}e^{-\beta E} \, dE,$

Hence: $N = \dfrac{C}{\beta^{3/2}} \int_0^\infty (\beta E)^{1/2} e^{-\beta E} \, d(\beta E)$.

Let $\beta E \equiv x$ so: $N = \dfrac{C}{\beta^{3/2}} \int_0^\infty x^{1/2} e^{-x} \, dx$.

From the integral tables this is: $\Gamma(3/2)$.

But $\Gamma(3/2) = (1/2)\Gamma(1/2)$ and $\Gamma(1/2) = \sqrt{\pi}$.

So, $N = \dfrac{C}{2\beta^{3/2}} \sqrt{\pi}$.

Hence, $C = 2\pi N \left(\dfrac{\beta}{\pi}\right)^{3/2} = \dfrac{2\pi N}{(\pi kT)^{3/2}}$.

d. Note that the last line below is "as stated" in MISN-0-157:

$$
\begin{aligned}
E_{ave} &= \frac{1}{N} \int_0^\infty E \frac{dn}{dE} \, dE = \frac{C}{N} \int_0^\infty E \, E^{1/2} e^{-\beta E} \, dE \\
&= \frac{C}{N} \int_0^\infty E^{3/2} e^{-\beta E} \, dE = \frac{C}{N\beta^{5/2}} \int_0^\infty (\beta E)^{3/2} e^{-\beta E} \, d(\beta E) \\
&= \frac{C}{N\beta^{5/2}} \int_0^\infty x^{3/2} e^{-x} \, d(x) = \frac{C}{N\beta^{5/2}} \, \Gamma(5/2) \\
&= \frac{C}{N\beta^{5/2}} \frac{3}{2} \frac{1}{2} \Gamma(1/2) = \frac{2\pi N}{(\pi kT)^{3/2}} \frac{1}{N} (kT)^{5/2} \frac{3}{2} \frac{1}{2} \sqrt{\pi} \\
&= \frac{3}{2} kT \, .
\end{aligned}
$$

Acknowledgments

MISN-0-? Graphics Backup cover

$\dfrac{dn}{dE}$

E

Fig 1

$\dfrac{dn}{dE}$

E

Fig 2

$\dfrac{dn}{dE}(E_0)$

$\dfrac{dn}{dE}(E)$

E → E_0

Fig 3

$\dfrac{dn}{dE}(E_0)$ ΔE

LOCAL GUIDE

The readings for this unit are on reserve for you in the Physics-Astronomy Library, Room 230 in the Physics-Astronomy Building. Ask for them as "The readings for CBI Unit 159." Do **not** ask for them by book title.

PROBLEM SUPPLEMENT

1. In a dilute gas containing very many molecules, such that there is a continuous distribution of energies among the molecules, the Maxwell-Boltzmann distribution law is satisfied:

$$\frac{dn}{dE} = \frac{2\pi N}{(\pi kT)^{3/2}} E^{1/2} \, e^{-E/kT} \ .$$

Identify the terms in this relation, explain what it tells you and plot a rough sketch of this function, labeling axes. [K] What is the partition of this system? [I] How is (dn/dE) related to N? [A]

2. Consider the following fictitious system. There are 10^{20} particles in the system. Some 3×10^{19} of these particles have an energy of $0.06\,\text{eV}$, 3×10^{19} of them have an energy of $0.03\,\text{eV}$, while 4×10^{19} of them have an energy of $0.04\,\text{eV}$.

   a. What is the partition of this system? [E]

   b. What is the total internal energy of this system in eV? [B] In joules? [L]

   c. What is the average energy of the particles of this system? [G]

3. How does the partition of the above system differ from the partition of a real dilute gas of 10^{20} particles? [C]

4.
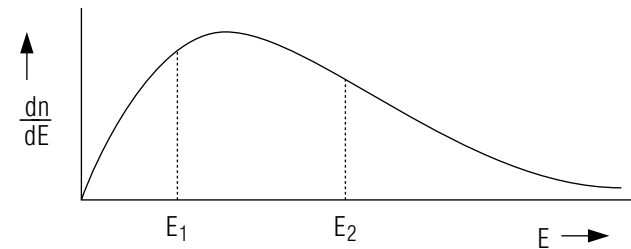
Above is shown the plot of the distribution function (number of molecules per unit energy interval plotted versus the energy) for a gas at a temperature T.

   a. What is the total number of particles which at any instant have an energy between E_1 and E_2 (Express your answer graphically)? [J]

b. Again in terms of the graph, what is the total number of particles in this gas? [F]

5. Starting from the Maxwell-Boltzmann distribution law, calculate the average energy of a molecule of an ideal gas. [H]

6. Starting from the Maxwell-Boltzmann distribution law, calculate the RMS value of the energy of a molecule of an ideal gas. [Find first the average value of E^2.) [D]

Brief Answers:

A. $N = \int_0^\infty \dfrac{dn}{dE} \, dE$.

B. $U = 4.3 \times 10^{18}$ eV.

C. This is only one partition, one with extremely low probability. The most probable partition is the Boltzmann distribution for this total number of particles, with this E_{ave}.

D. $E_{RMS} = \dfrac{1}{2}\sqrt{15}\, kT$.

E. The partition is the set of 3 numbers n_1, n_2, n_3.

F. The total area under the curve.

G. $E_{ave} = 4.3 \times 10^{-2}$ eV$= 6.9 \times 10^{-21}$ joules.

H. See Exercise D, part (d). $E_{ave} = (3/2)\, kT$.

I. $(dn/dE)\, dE$ is the number of particles with energy between E and $E + dE$.

   The set of all these numbers for all E is the partition. The partition is essential to the distribution function.

J. The area under the curve between E_1 and E_2.

K. See the discussion in this Unit.

L. 0.69 joules.