UNIVERSITY OF AGRICULTURE, ABEOKUTA, NIGERIA

DEPARTMENT OF PHYSICS

PHS 321: STATISTICAL AND THERMAL PHYSICS

BY

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1: Statistical description of systems of particles

Consideration of non interactive systems of particles to analyze the probability with binomial and Gaussian distribution by consideration of the statistical approach and with the density of systems of particles.

1: Statistical Description of Systems of Particles:
- ➢ Statistical Theories,
- ➢ Ensemble
- ➢ Accessible state
- ➢ Probability calculation
- ➢ Phase space

1.1 Specification of the state of the system

How do we determine the state of a many particle system? Well, let us, first of all, consider the simplest possible many particle system, which consists of a single spinless particle moving classically in one dimension. Assuming that we know the particle's equation of motion, the state of the system is fully specified once we simultaneously measure the particle's position q and momentum p. In principle, if we know q and p then we can calculate the state of the system at all subsequent times using the equation of motion

1.2 Statistical ensemble

If we are informed about any of the initial conditions of a thrown up coin like its position, the height of the throw and the corresponding velocity of the coin, we would indeed predict the out come of the experiment by applying the law of classical mechanics.

In an experiment that describes the outcome in terms of the probability of a single coin, we consider an ensemble consisting of many such single experiments.

1.3 Probability

In this section we will discuss some of elementary aspect of probability theory. It is important to keep in mind that whenever it is desired to described a situation from a statistical point of view (i.e., in terms of probabilities), It is always necessary to consider an assembly (ensemble) consists of a very large number of similar prepared systems.

Group discussion

Give some example which can be described by two states of systems of particles

Answer

a) In throwing a pair of dice, one gives a statistical description by considering a very large number.

b) In the basic probability concept, it will be useful to keep in mind a specific simple but important, illustrative example the so called random walk problem

c) Magnetism: An atom has a spin $\frac{1}{2}$ and a magnetic moment μ; in accordance with quantum mechanics, its spin can therefore point either "up" or "down" with respect to a given direction. If both these possibilities are equally likely, what is the net total magnetic moment of N such atoms?

d) Diffusion of a molecule in a gas: A given molecule travels in three dimensions a mean distance l between collisions with other molecules. How far is it likely to have gone after N collisions?

1.4 The simple random walk problem in one dimension

For the sake of simplicity we shall discuss the random walk problem in one dimension. A particle performing successive steps, or displacements, in one dimension after a total of N such steps, each of length l, the particle is located at

$$x = ml \quad \text{Where } m \text{ is an integer lying between } N \leq m \leq N$$

The probability P_N (m) of finding the particle at the position $x = ml$ after N such steps.

$$W_N(n_1) = \frac{N!}{n_1! n_2!} p^{n_1} q^{n_2}$$

Group discussion

Derive the probability $W_N(n_1)$ for finding the particle at position x=ml after N steps

You can see the derivation as follow

The total number of steps N is simply

$$N = n_1 - n_2$$

The net displacement where

$$m = n_1 - n_2$$

$$m = n_1 - n_2 = n_1 - (N - n_1) = 2n_1 - N$$

Our fundamental assumption was that successive steps are statistically independent of each other. Thus one can assert simply that, irrespective of past history, each step is characterized by the respective probabilities

P = probability that the step is to the right

q = 1 − p = probability that the step is to the left

Now, the probability of any one given sequence of n_1 steps to the right and n_2 steps to the left is given simply by multiplying the respective probabilities, i.e., by

$$p_1 p_2 p_3 \cdots p_n q_1 q_2 q_3 \cdots q_n = p^{n_1} q^{n_2}$$

The number of distinct possibilities is given by

$$\frac{N!}{n_1! n_2!}$$

The probability $W_N(n_1)$ of taking n_1 steps to the right and $n_2 = N - n_1$ steps to the left, in any order, is obtained by multiplying the probability of this sequence by the number of possible sequences of such steps. This gives

$$W_N(n_1) = \frac{N!}{n_1! n_2!} p^{n_1} q^{n_2}$$

1.5 Binomial Distribution

Indeed, we recall that the binomial expansion is given by the formula

$$(p + q)^N = \sum_{n=0}^{N} \frac{N!}{n!(N-n)!} p^n q^{N-n}$$

Read the binomial distribution in the fundamentals of thermodynamics book (Federick Reif) pp.7-23

Group discussion

Given that $n_1 = \frac{1}{2}(N + m)$, $\qquad n_2 = \frac{1}{2}(N - m)$

Show that

$$p_N(m) = \frac{N!}{[(N+m)/2]![(N-m)/2]!}\left(\frac{1}{2}\right)^N$$

In this discussion you may consider the probability $P_N(m)$ that the particle is found at position m

after N steps is the same as $W_N(n_1)$ given by

$$P_N(m) = W_N(n_1)$$

1.5.1 Mean Value

If f(u) is any function of u, then the mean value of f(u) is defined by

$$\overline{f(u)} \equiv \frac{\sum_{i=1}^{M} p(u_i)f(u_i)}{\sum_{i=1}^{M} P(u_i)}$$

This expression can be simplified. Since P(u$_i$) is defined as a probability, the quantity

$$P(u_1) + P(u_2) + ... + P(u_M) \equiv \sum_{i=1}^{M} P(u_i)$$

$$\sum_{i=1}^{M} P(u_i) = 1 \qquad \text{This is the so-called "normalization condition"}$$

$$\overline{f(u)} \equiv \sum_{i=1}^{M} p(u_i)f(u_i)$$

Activity

Derive the summation and the product of the mean value of different function

Solution

If f(u) and g(u) are any two functions of u, then

$$\overline{f(u)\_g(u)} = \sum_{i=1}^{M} P(u_i)[f(u_i) + g(u_i)] = \sum_{i=1}^{M} P(u_i)f(u_i) + \sum_{i=1}^{M} P(u_i)g(u_i)$$

Or

$$\overline{f(u) + g(u)} = \overline{f(u)} + \overline{g(u)}$$

If c is any constant, it is clear that

$$\overline{cf(u)} = \overline{cf(u)}$$

1.5.2 Deviation dispersion and standard deviation

$\Delta u = u - \overline{u}$ deviation

$$\overline{(\Delta u)^2} \equiv \sum_{i-1}^{M} P(u_i)(u_i - \overline{u})^2 \geq 0 \quad \text{second moment of u about its mean," or more simply the}$$

"dispersion of u" since $((\Delta u)^2 \geq 0$ can never be negative,

The variance of u is proportional to the square of the scatter of u around its mean value. A more useful measure of the scatter is given by the square root of the variance,

$$\Delta * u = \left[\overline{(\Delta u)^2}\right]^{\frac{1}{2}} \quad \text{which is usually called the standard deviation of u.}$$

1.6 The Gaussian Distribution

$$P(n) \cong \frac{1}{\sqrt{2\pi}\Delta * n_1} \exp\left[-\frac{\left(n - \overline{n_1}\right)^2}{2\left(\Delta * n_1\right)^2}\right]$$

This is the famous Gaussian distribution function. The Gaussian distribution is only valid in the limits N>>1 and $\overline{n_1} >> 1$

Activity

Using the Taylor expansion and derive the Gaussian distribution

Solution

Let us expand lnP around $n = \tilde{n}$. Note that we expand the slowly varying function lnP(n), instead of the rapidly varying function P(n), because the Taylor expansion of P(n) does not converge sufficiently rapidly in the vicinity of n = $\tilde{n}$ to be useful. We can write

$$\ln P(\tilde{n} + n) = \ln P(\tilde{n}) + \eta B_1 + \frac{\eta^2}{2} B_2 + \dots$$

where

$$B_k = \frac{d^k \ln P}{dn^k}\Bigg|_{n=\bar{n}}$$

$$P(n) \cong P(\overline{n_1})\exp\left[-\frac{(n-\overline{n_1})^2}{2(\Delta * n_1)^2}\right]$$

The constant $P(\overline{n_1})$ is most conveniently fixed by making use of the normalization condition

For discrete case

$$\sum_{n_1=0}^{N} P_N(n_!) = 1$$

For continues case

$$\int_0^N P_N(n)dn = 1$$

for a continuous distribution function. Since we only expect P (n) to be significant when n lies in the relatively narrow range $\overline{n_1} \pm \Delta * n_1$, the limits of integration in the above expression can be replaced by $\pm\infty$ with negligible error. Thus,

$$P(\overline{n})\int_{-\infty}^{\infty}\exp\left[-\frac{(n-\overline{n_1})^2}{2(\Delta * n_1)^2}\right]dn = P(\overline{n_1})\sqrt{2}\Delta * n_1 \int_{-\infty}^{\infty}\exp(-x^2)dx \cong 1$$

1.7 The principle of equal a priori probabilities

Activity

Take a bottle of gas which is isolated with the external environment.
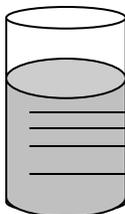
Solution

In this situation, we would expect the probability of the system being found in one of its accessible states to be independent of time.

This implies that the statistical ensemble does not evolve with time.

Individual systems in the ensemble will constantly change state; but the average number of systems in any given state should remain constant.

Thus, all macroscopic parameters describing the system, such as the energy and the volume, should also remain constant.

There is nothing in the laws of mechanics which would lead us to suppose that the system will be found more often in one of its accessible states than in another. We assume, therefore, that the system is equally likely to be found in any of its accessible states. This is called the assumption of equal a priori probabilities, and lies at the very heart of statistical mechanics.

1.8 The relaxation time

Activity

Take an isolated many particle systems will eventually reach equilibrium, irrespective of its initial state.
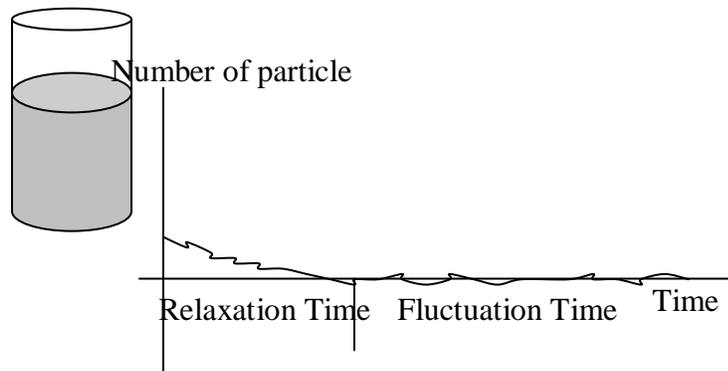
Solution

The typical time-scale for this process is called the relaxation time, and depends in detail on the nature of the inter-particle interactions.

The principle of equal a priori probabilities is only valid for equilibrium states.

The relaxation time for the air in a typical classroom is very much less than one second. This suggests that such air is probably in equilibrium most of the time, and should, therefore, be governed by the principle of equal a priori probabilities.

1.8 Behavior of the density of states

A macroscopic system is one which has many degrees of freedom denote the energy of the system by E. We shall denote by $\Omega(E)$ the number of states whose energy lies between E and E+dE in a system. Let $\phi(E)$ denote the total number of possible quantum states of the system which are characterized by energies less than E. Clearly $\phi(E)$ increase when E increases. The number of states $\Omega(E)$ in the range between E and E+dE is then

$$\Omega(E) = \phi(E + \delta E) + \phi(E) = \frac{\partial \phi}{\partial E} \partial E$$

Activity

Consider the case of a gas of N identical molecules enclosed in container of volume V. The energy of the system can be written

$$E = K + U + E_{int} \quad \text{Where}$$
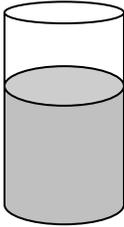
$$K = K(p_1, p_2, \ldots p_N) = \frac{1}{2m} \sum_{i=1}^{N} p_i^2 \, , \, U = U(r_1, r_2, \ldots r_N)$$

Considering the system for mono atomic ideal gas

$$U = 0, \quad E_{int} = 0$$

Solution

The number of states Ω (E, V) lying between the energies E and E+ δ E is simply equal to the number of cells in phase-space contained between these energies.
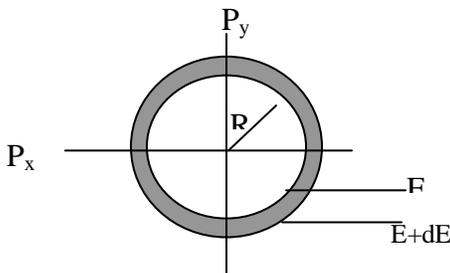
In other words, Ω (E, V) is proportional to the volume of phase-space between these two energies:

$$\Omega(E,V) \propto \int_{E}^{E+\delta E} d^3 r_1 \ldots d^3 r_N \, d^3 p_1 \ldots d^3 p_N$$

Here, the integrand is the element of volume of phase-space, with

$d^3 r = dx_i \, dy_i \, dz_i$

$d^3 p = dp_{i\,x} \, dp_{i\,y} \, dp_{i\,z}$,

the number of states $\Omega(E)$ lying spherical shell between energies E and E+dE is given

$$\Omega = BV^N E^{3N/2}$$

In other words, the density of states varies like the extensive macroscopic parameters of the system raised to the power of the number of degrees of freedom. An extensive parameter is one which scales with the size of the system (e.g., the volume). Since thermodynamic systems generally possess a very large number of degrees of freedom, this result implies that the density of states is an exceptionally rapidly increasing function of the energy and volume. This result, which turns out to be quite general, is very useful in statistical thermodynamics.

Problem

1. A penny is tossed 400 times. Find the probability of getting 215 heads. (Suggestion: use the Gaussian approximation)

Solution

A penny is tossed 400 times. Find the probability of getting 215 heads is given by the Gaussian approximation

$$P(n) \cong \frac{1}{\sqrt{2\pi}\Delta * n_1} \exp\left[-\frac{(n - \overline{n_1})^2}{2(\Delta * n_1)^2} \right]$$

where

N=400, n_1=251, p=1/2, q=1/2

$$\overline{n_1} = Np \qquad \Delta * n_1 = \sqrt{Npq} = \sqrt{400 x 1/2 x 1/2} = \sqrt{100} = 10$$

$$(\Delta * n_1)^2 = 100, \quad \overline{n_1} = 200$$

Substituting in the Gaussian equation

$$P(251,400) = \frac{1}{10\sqrt{2\pi}} e^{-\frac{(251-200)^2}{200}}$$

$P(251,400) \cong 1.3x10^{-2}$

Problem

2. A particle of mass m is free to move in one dimension. Denote its position coordinate by x and its momentum by p. Suppose that this particle is confined with a box so as to be located between x=0 and x=L, and suppose that its energy is known to lie between E and E+dE. Draw the classical phase space of this particle, indicating the regions of this space which are accessible to the particle

Solution

Let us represent the particle motion in the coordinate of p, x
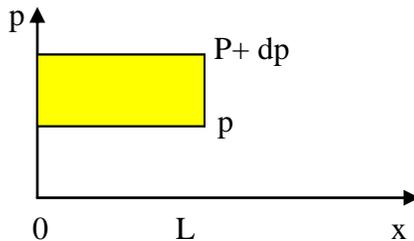
The particle with position x and momentum p position lies between x=0 and x=L, energy lies between E and E+dE

The momentum of the particle is given by

$E=p^2 /2m$

$p = \sqrt{2mE}$

the accessible state in the phase space $\Omega(E) = \dfrac{d\phi(E)}{dE} \delta E$ the number of states which have an

energy E in phase space is given by $\phi(E) = p = \sqrt{2mE}$

3. What is the probability of throwing a three or a six with one throw of die?

solution

the probability that the face exhibit either 3 or 6 is $\dfrac{1}{6}+\dfrac{1}{6}=\dfrac{1}{3}$

2: Macroscopic Parameters and their Measurements

Introduction to the Activity

The laws that govern the relationships between heat and work are studied in thermal physics. Since heat is a form of energy and work is the mechanism by which energy is transferred, these laws are based on the basic principles that govern the behaviour of other types of energy such as the principle of conservation of energy.

In this activity you will be guided through a series of tasks to understand heat as a form of energy and define terms like heat capacity, heat of fusion and heat of vaporization.

Detailed Description of the Activity (Main Theoretical Elements)
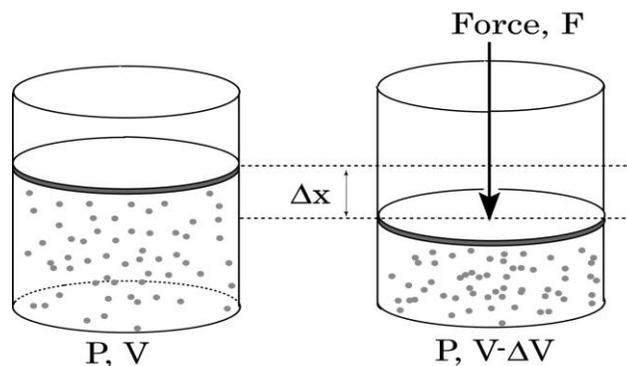
Figure: compression of gas molecules

Macroscopic Measurements:

➢ Work and internal energy

➢ Absolute temperature

➢ Heat capacity and specific heat capacity

➢ Entropy

2.1 Work and internal energy

The macroscopic work done by a system is determined by the volume of a system if changed quasi-statically from V_i to V_f and throughout this process the mean pressure of the system has the measurable value $\overline{p}(V)$.

$$W = \int_{V_i}^{V_f} \overline{p}\,dV$$

If the system is isothermally insulated so it can't absorb any heat then Q=0

The internal energy $\Delta \overline{E} = -W$

Activity

Consider a system that consists of the cylinder containing a gas. Supply the external energy to the system by switching the circuit. What do you observe? Consider a standard macrostate i of volume V_i and mean pressure $\overline{p}_i$, where $\overline{E} = \overline{E}_i$. How would one determined the mean energy $\overline{E}_j$ of any other macrostate j of volume V_j and the mean pressure $\overline{p}_j$?

Figure A system consists of cylinder containing gas.
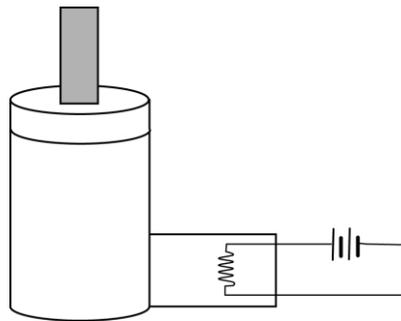
The volume V of the gas is determined by the position of the piston. The resistance can brings thermal contact to the system.

Solution

The microstate of the system can be specified by the two parameters, volume V and internal
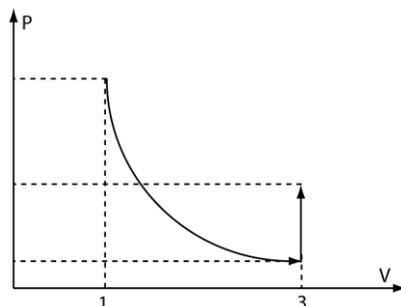
energy $\overline{E}$. Each macrostate can be represented by a point on $\overline{pV}$ diagram.

As the gas expand from 1 to its final volume 3 the mean pressure decrease to some value $\overline{p_3}$ and the work done by the piston W_{13}

To bring the pressure $\overline{p_3}$ without changing the volume, work is done by the electric resistance by an amount W_R and if the $\Delta \overline{\varepsilon}$ amount of energy consumed by the resistance then the energy supplied by the external system is $W_R - \Delta \overline{\varepsilon}$.

The total internal energy of the system in state in state 2 is then given by

$$\overline{E} = \overline{E}_a - W_{ac} + (W_R - \Delta \overline{\varepsilon})$$

The amount of heat absorbed from a macrostate 1 to a macrostate 2 is given by

$$\overline{E}_2 = (\overline{E}_2 - \overline{E}_1) + W_{12}$$

Heat

The heat Q_{ab} absorbed by the system in going from a macrostate a to another macrostate is given by

$$Q_{ab} = \left(\overline{E}_b - \overline{E}_a \right) + W_{ab}$$

2.2 Absolute temperature

Properties of absolute temperature

1. The absolute temperature provides one with a temperature parameter which is completely independent of the nature of the particular thermometer used to perform the temperature measurement.

2. The absolute temperature T is a parameter of fundamental significance which enters all the theoretical equations. Hence all the theoretical predictions will involve this particular temperature.

Activity

From the equation of state $\bar{p} = \dfrac{N}{V}kT = nkT$

2.3 Heat capacity and specific heat

Consider a macroscopic system whose macrostate can be specified by its absolute temperature T and some other macroscopic parameter y (y might be volume or mean pressure)

Activity

➢ Take a macroscopic system at temperature T, an infinitesimal amount of heat dQ is added to the system and the other parameters y kept fixed.

➢ The resulting change dT in temperature of the system depends on the nature of the system as well as on the parameters T and y specifying the macrostate of the system

Result

The specific heat capacity at constant y is defined by

$$C_y = \left(\frac{dQ}{dT}\right)_y$$

The specific heat per mole or heat capacity per mole is thus defined by

$$c_y = \frac{1}{v}C_y = \frac{1}{v}\left(\frac{dQ}{dT}\right)_y$$

Eventually the specific heat per gram is defined as

$$c'_y = \frac{1}{m}C_y = \frac{1}{m}\left(\frac{dQ}{dT}\right)_y$$

Task

Take a gas or a liquid whose macrostate can be specified by two parameters say the temperature T and volume. Calculate the heat capacity at constant volume C_v and at constant pressure C_p
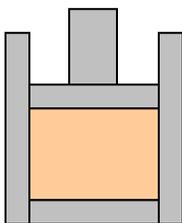
Figure Diagram illustrated specific heat measurement of a gas kept at constant volume or at constant pressure

1. **To determine** C_v

We clamp the piston in position that the volume of the system is kept fixed.

In this case the system cannot do any work, and the heat dQ added to the system goes entirely to increase the internal energy of the system

$$dQ = d\bar{E}$$

2. **To determine** C_p

The piston left completely free to move the weight of the piston being equal to the constant force per unit area (mean pressure) on the system

In this case the piston will move when heat dQ is added to the system; as the result the system does also mechanical work. Thus the heat dQ is used both to increase the internal energy of the system and to do mechanical work on the piston

$$dQ = d\bar{E} + \bar{p}dV$$ which is the fundamental law of thermodynamics

From the result we expected

i). $d\bar{E}$ is increase by small amount(and hence the temperature T will also increase by smaller amount) in the second case compared to the first.

ii). $C_p > C_v$

2.3.1 Heat capacity using the second law of thermodynamics

The second law of thermodynamics is given by $dQ = TdS$ the heat capacity

$$C_y = T\left(\frac{\partial S}{\partial T}\right)_y$$

If all external parameters of the system kept constant, then the system dose no macroscopic work,

$dW = 0$ then the first law reduced to $dQ = d\bar{E}$

$$C_V = T\left(\frac{\partial S}{\partial T}\right)_V = \left(\frac{\partial \bar{E}}{\partial T}\right)_V$$

Example

Let us consider heat measurements by the method of mixtures in terms of the specific heats of the substance involved. Consider that two substances A and B, of respective masses m_A and m_B, are brought into thermal contact under condition where the pressure is kept constant. Assume that before the substance are brought into thermal contact their respective equilibrium temperature are T_A and

T_B respectively. Compute the final temperature T_f

Solution

2.4 Entropy

The entropy can readily be determined by using the second law $dQ = TdS$ for an infinitesimal quasi-static process.

Given any macrostate b of the system, one can find the entropy difference between this state and some standard state a to state b and calculating for this process

$$S_b - S_a = \int_a^b \frac{dQ}{T}$$

Suppose that the macrostate of a body is specified by its temperature, since all its other parameters are kept constant.

$$S(T_b) - S(T_a) = \int_a^b \frac{dQ}{T} = \int_{T_a}^{T_b} \frac{C_y(T')dT'}{T'}$$

then

$$S(T_b) - S(T_a) = C_y \ln \frac{T_b}{T_a}$$

Problem

Consider two system A and system B with constant specific heat C'_A and C'_B and originally at

respective temperature T_A and T_B, are brought into thermal contact with each other. After the system

come to equilibrium, they reach a come final temperature T_f. What is the entropy change of the

entire system in this process?

System A,T$_A$ B,T$_B$ System

Isolated system
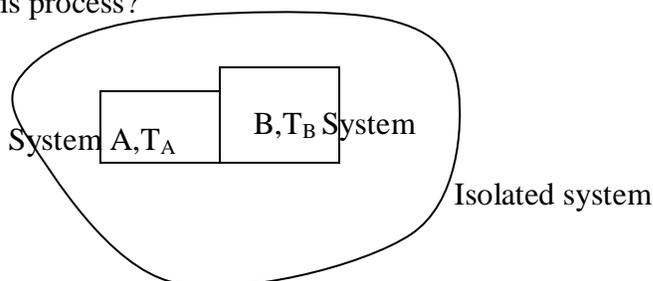
Answer

To calculate the entropy change of system A, we can imagine that it is brought from its initial temperature T_A to its final temperature T_f by a succession of infinitesimal heat additions.

$$dQ = m_A C'_A dT$$

$$dS = \frac{dQ}{T} = S_A(T_f) - S_A(T_A) = \int_{T_A}^{T_f} \frac{m_A C_A' dT}{T} = m_A C'_A \ln\frac{T_f}{T_A}$$

Similarly for the system B

$$dS = \frac{dQ}{T} = S_B(T_f) - S_B(T_B) = \int_{T_B}^{T_f} \frac{m_B C_B' dT}{T} = m_B C'_B \ln\frac{T_f}{T_B}$$

The total entropy change

$$\Delta S_A + \Delta S_B = m_A C'_A \ln\frac{T_f}{T_A} + m_B C'_B \ln\frac{T_f}{T_B}$$

Problems

(a) One kilogram of water at 0^0C is brought into contact with a large heat reservoir at 100^0C. When the water has reached 100^0C, what has been the change in entropy of the water? Of the heat reservoir? Of the entire system consisting of both water and heat reservoir?

b) If the water had been heated from 0^0C to 100^0C by first bringing it is contact with a   reservoir at 50^0C and then with a reservoir at 100^0C, what would have been the change in entropy of the entire system?

C) Show how the water might be heated from 0^0C to 100^0C with no change in the entropy of the entire system.

Answer

Entropy of water

$$dS_{0\to100^0 C} = \frac{dQ}{T} \quad \text{where} \quad dQ = mCdT$$

$$= \frac{mCdT}{T}$$

$$\Delta S = mC \int_{273k}^{373k} \frac{dT}{T}$$

$$\Delta S = mC \ln \frac{T_f}{T_i}$$

$$\Delta S_{water} = mC \ln \frac{373}{273} \quad \text{(where mass of water =1kg)}$$

$$= 1310 J/K$$

The entropy of reservoir

The amount of heat loss by the reservoir

$$\Delta Q_{water} = -\Delta Q_{reservoir}$$

$$\Delta Q_{reservoir} = -mC(T_f - T_i)$$

$$\Delta S_{reservoir} = -\frac{mC(T_f - T_i)_{water}}{T_{373}}$$

$$= -1126 J/K$$

Total entropy

$$\Delta S_{total} = \Delta S_{reservoir} + \Delta S_{water}$$

$$\Delta S_{total} = -\frac{mC(T_f - T_i)_{water}}{T_{373}} + mC \ln \frac{373}{273}$$

$$\Delta S_{total} = 184 J/K$$

3: Statistical Thermodynamics

Introduction to the Activity

The Ideal Gas Law describes the relationship between pressure, volume, the number of atoms or molecules in a gas, and the temperature of a gas. This law is an idealization because it assumes an "ideal" gas. An ideal gas consists of atoms or molecules that do not interact and that occupy zero volume.

A real gas consists of atoms or molecules (or both) that have finite volume and interact by forces of attraction or repulsion due to the presence of charges. In many cases the behaviour of real gases can be approximated quite well with the Ideal Gas Law. and this activity focuses on the description of an ideal gas.

3.1 Equilibrium conditions and constraints

Consider an isolated system whose energy is specified to lie in a narrow range. As usually, we denote by Ω then number of states accessible to this system. From the fundamental postulate we know that in equilibrium such a system is equally likely to be found in any one of these states. If a system has a constraint $y_1, y_2, \ldots y_n$ then the accessible state given by $\Omega = \Omega(y_1, y_2, \ldots y_n)$.

If some constraints of an isolated system are removed, the parameters of the system tend to readjust themselves in such a way that $\Omega = \Omega(y_1, y_2, \ldots y_n)$ approaches a maximum $\Omega_f \geq \Omega_i$

3.2 Thermal interaction between macroscopic systems

Activity

Consider a purely thermal interaction between two macroscopic systems, A and A',
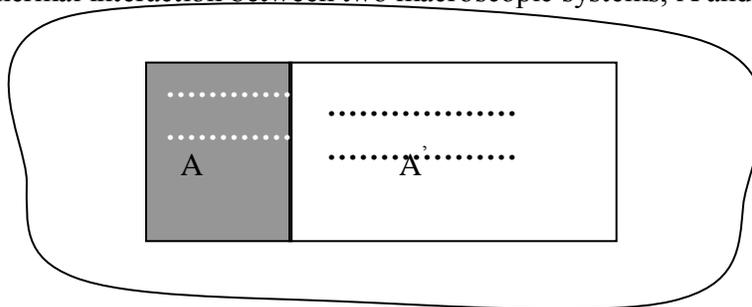
Energy of the systems E and E', the external parameters are constant, so that A and A' cannot do work on one another and the systems are thermally contact heat will exchange. Considering the energy width δE

➢ Let us calculate the accessible state

➢ The temperature at equilibrium

➢ The entropy at equilibrium

Result

The number of microstates of A consistent with a macrostate in which the energy lies in the range E to E + δ E is denoted Ω (E). Likewise, the number of microstates of A' consistent with a macrostate in which the energy lies between E' and E' + δ E is denoted Ω '(E).

The combined system $A^{(0)}$ = A + A' is assumed to be isolated (i.e., it neither does work on nor exchanges heat with its surroundings). The number of accessible to the entire system A^0 let us denote by Ω^0 (E) when A has energy between E and E+dE.

The probability

P(E)=CΩ^0(E)

Total accessible state

$$\Omega^0(E) = \Omega(E)\Omega'(E^0 - E)$$

Temperature at equilibrium

The probability of system A having the energy an energy near E is given by

$$P(E)=C\Omega(E)\Omega'(E^0 - E)$$

To locate the maximum position of P(E) at E=$\tilde{E}$

$$\frac{\partial \ln P(E)}{\partial E} = \frac{1}{P}\frac{\partial P}{\partial E} = 0$$

$$\ln P(E) = \ln C + \ln \Omega(E) + \ln \Omega'(E')$$

$$\frac{\partial \ln P(E)}{\partial E} = \frac{\partial \ln \Omega(E)}{\partial E} + \frac{\partial \ln \Omega'(E')}{\partial E} = 0$$

where E^0=E+E' which is dE=-dE' then

$$\frac{\partial \ln \Omega(E)}{\partial E} - \frac{\partial \ln \Omega'(E')}{\partial E'} = 0$$

$$\beta(\tilde{E}) = \beta'(\tilde{E'})$$

Entropy of the combined system

Activity

where $\tilde{E}$ and $\tilde{E}'$ denote the corresponding energies of A and A' at the maximum, and where we have introduced the definition

$$\beta(E) = \frac{\partial \ln \Omega}{\partial E} \quad kT \equiv \frac{1}{\beta} \quad \text{where k is some positive constant having the dimension of energy and whose}$$

magnitude in some convenient arbitrary way.

The parameter T is then defined as $kT = \dfrac{\partial S}{\partial E}$

Solution

Where we have introduced the definition $S \equiv k \ln \Omega$ this quantity S is given the name of entropy

Total accessible state $\Omega^0(E) = \Omega(E)\Omega'(E^0 - E)$ and taking the logarithm

$$\ln \Omega^0(E) = \ln \Omega(E) + \ln \Omega'(E^0 - E)$$

$$S^{(0)} = S + S'$$

The condition of maximum probability is expressible as the condition that the total entropy
$S + S' = \max imum$ entropy occurs when T=T'

3.3 The approach to thermal equilibrium

If the two systems are subsequently placed in thermal contact, so that they are free to exchange heat energy until the two systems attain final mean energies $\overline{E}_f$ and $\overline{E}_f'$

which are

$$\beta_f = \beta_f'$$

It follows from energy conservation that

$$\overline{E}_f + \overline{E}'_f = E_i + E_i'$$

The mean energy change in each system is simply the net heat absorbed, so that

$$Q \equiv \overline{E}_f - E_i \; ; \qquad Q' \equiv \overline{E}'_f - E'_i$$

The conservation of energy then reduces to

Q+Q'=0:

It is clear, that the parameter β, defined

$$\beta = \frac{\partial \ln \Omega}{\partial E}$$

Temperature

1. If two systems separately in equilibrium are characterized by the same value of the parameter, then the systems will remain in equilibrium when brought into thermal contact with each other.

2. If the systems are characterized by different values of the parameter, then they will not remain in equilibrium when brought into thermal contact with each other.

If two systems are n thermal equilibrium with a third system, then they must be in thermal equilibrium with each other

3.4 Heat reservoir
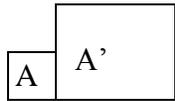
If A' is sufficiently large compared to A so A' is a reservoir.

Suppose the macroscopic system A' has $\Omega'(E')$ accessible states and absorbs heat $Q' = \Delta E'$ using

Expanding $\ln \Omega'\left(E', Q'\right)$ at E'=Q

$$\ln \Omega'(E', Q') - \ln \Omega'(E') = \left(\frac{\partial \ln \Omega'}{\partial E'}\right) Q' + \frac{1}{2}\left(\frac{\partial^2 \ln \Omega'}{\partial E'^2}\right) Q'^2 + \dots$$

using approximation

$$\left(\frac{\partial \ln \Omega'}{\partial E'}\right) Q' = \frac{Q'}{kT'} \quad \text{the higher order becomes zero}$$

$$\ln \Omega'(E', Q') - \ln \Omega'(E') = \frac{Q'}{kT'}$$

$$k\Delta(\ln \Omega'(E', Q') - \ln \Omega'(E')) = \frac{\Delta Q'}{T'}$$

$\Delta S' = \dfrac{\Delta Q'}{T'}$ For a heat reservoir

3.5   *Dependence of the density of states on the external parameter*

<u>**Activity**</u>

Now that we have examined in detailed the thermal interaction between systems, let us turn to the general case where mechanical interaction can also take place, i.e. where the external parameters of the systems are also free to exchange. We begin, therefore, by investigating how the density of states depends on the external parameters.

<u>**Solution**</u>

Figure shaded area indicate the energy range occurred by states with a value of whose energy changes from E to E+when the external parameter is changed from x to x+dx
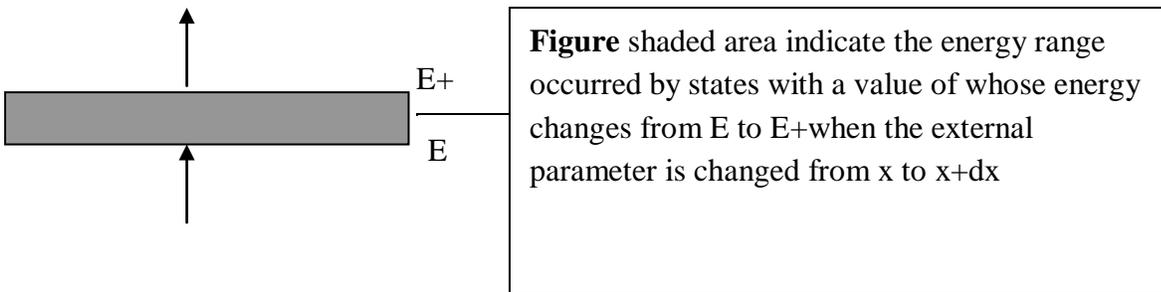
The number of states accessible to the system microstates accessible to the system when the overall energy lies between E and E + δ E depends on the particular value of x, so we can write

$$\Omega \equiv \Omega(E, x).$$

The number of states σ (E, x) whose energy is changed from a value less than E to a value greater than E when the parameter changes from x to x + dx is given by the number of microstates per unit energy range multiplied by the average shift in energy of the microstates, Hence

$$\sigma(E, x) = \frac{\Omega(E, x)}{\delta E} \overline{\frac{\partial E_r}{\partial x}} dx$$

where the mean value of $\partial E_r / \partial x$ is taken over all accessible microstates (i.e., all states where the energy lies between E and E + δ E and the external parameter takes the value x). The above equation can also be written

$$\sigma(E, x) = -\frac{\Omega(E, x)}{\delta E} \overline{X} dx$$

where

$\overline{X}(E,x) = -\dfrac{\overline{\partial E_r}}{\partial x}$ is the mean generalized force conjugate to the external parameter x.

Consider the total number of microstates between E and E + δ E. When the external parameter changes from x to x + dx, the number of states in this energy range changes by $\left(\dfrac{\partial \Omega}{\partial x}\right)dx$. In symbols

$$\dfrac{\partial \Omega(E,x)}{\partial x}dx = \sigma(E) - \sigma(E + \delta E) \cong \dfrac{\partial \sigma}{\partial E}\delta E$$

which yields

$$\dfrac{\partial \Omega}{\partial x} = \dfrac{\partial(\Omega \overline{X})}{\partial E}$$

$$\dfrac{\partial \Omega}{\partial x} = \dfrac{\partial(\Omega \overline{X})}{\partial E} = \dfrac{\partial \Omega}{\partial E}\overline{X} + \Omega \dfrac{\partial \overline{X}}{\partial E} \qquad \text{then}$$

$$\dfrac{\partial \ln \Omega}{\partial x} = \dfrac{\partial \ln \Omega}{\partial E}\overline{X} + \dfrac{\partial \overline{X}}{\partial E}$$

$$\dfrac{\partial \ln \Omega}{\partial x} = \dfrac{\partial \ln \Omega}{\partial E}\overline{X} = \beta \overline{X}$$

Thus,

$$\dfrac{\partial \ln \Omega}{\partial x_\alpha} = \beta \overline{X}_\alpha$$

where $\overline{X}_\alpha$ is the mean generalized force conjugate to the parameter x_α

Infinitesimal quasi static process

Activity

Consider a quasi static process in which the system A, by virtue of its interaction with systems A',

is brought from an equilibrium state describe by $\bar{E}$ and $\bar{x}_\alpha$ $(\alpha = 1, 2, ...n)$ to an infinitesimally

different, equilibrium state described by $\bar{E} + d\bar{E}$ and $\bar{x}_\alpha + d\bar{x}_\alpha$.

What is the resultant change in the number of states Ω accessible to A?

Solution

The accessible state

$$\Omega = \Omega\left(E; x_1, ..., x_n\right)$$

$$d \ln \Omega = \frac{\partial \ln \Omega}{\partial E} d\bar{E} + \sum_{\alpha=1}^{n} \frac{\partial \ln \Omega}{\partial x_\alpha} d\bar{x}_\alpha$$

Substituting the in the above equation $\beta = \frac{\partial \ln \Omega}{\partial E}$, $\qquad \frac{\partial \ln \Omega}{\partial x_\alpha} = \beta \bar{X}_\alpha$

$$d \ln \Omega = \beta \left(d\bar{E} + \sum_\alpha \bar{X}_\alpha d\bar{x}_\alpha \right)$$

$$dW = \sum_\alpha \bar{X}_\alpha d\bar{x}_\alpha$$

Then $d \ln \Omega = \beta \left(d\bar{E} + dW \right) = \beta dQ$

The fundamental relation valid for any quasi-static infinitesimal process

$dQ = TdS = \left(d\bar{E} + dW \right)$ or equivalently

$$dS = \frac{dQ}{T}$$

Adiabatic process

$dQ = 0$ which asserts

$dS = 0$

Equilibrium

Consider the equilibrium between the systems A and A' in the simple case the external parameters are the volumes V and V' of the two systems. The number of state available to the combined system A^0 is given by the simple product.

$$\Omega^0(E,V) = \Omega(E,V)\Omega'(E',V')$$

Activity

Using the accessible state given for the combined system derive the equation that guarantee for thermal and mechanical equilibrium.

Solution

For the combined system the accessible state given as $\Omega^0(E,V) = \Omega(E,V)\Omega'(E',V')$

Taking the logarithm

$$\ln\Omega^0(E,V) = \ln\Omega(E,V) + \ln\Omega'(E',V')$$

The total entropy of the system given by

$$S^0 = S + S'$$

At the maximum value the total accessible state $d\ln\Omega^0 = 0$

$$d\ln\Omega^0(E,V) = d\ln\Omega(E,V) + d\ln\Omega'(E',V') = 0$$

$$d\ln\Omega = \frac{\partial\ln\Omega(E,V)}{\partial V}dV + \frac{\partial\ln\Omega(E,V)}{\partial E}dE + \frac{\partial\ln\Omega'(E',V')}{\partial V'}dV' + \frac{\partial\ln\Omega'(E',V')}{\partial E'}dE' = 0$$

where

$$\beta\bar{p} = \frac{\partial\ln\Omega(E,V)}{\partial V} \quad \text{similarly} \quad \beta'\bar{p}' = \frac{\partial\ln\Omega'(E',V')}{\partial V'}$$

$$\beta = \frac{\partial\ln\Omega(E,V)}{\partial E} \quad \text{similarly} \quad \beta' = \frac{\partial\ln\Omega'(E',V')}{\partial E'}$$

Substituting in the above equation

$$d\ln\Omega = \beta\bar{p}dV + \beta dE + \beta'\bar{p}'dV' + \beta'dE' = 0$$

from the combined system

$$E + E' = E^0$$

$$V + V' = V^0$$

Then $dE = -dE', \qquad dV = -dV'$

Substituting in the above equation

$$\beta \bar{p} dV + \beta dE - \beta' \bar{p}' dV - \beta' dE = 0$$

Collecting terms

$$\beta \bar{p} dV - \beta' \bar{p}' dV = 0$$

$$\beta dE - \beta' dE = 0$$

$$\beta dE = \beta' dE$$

Then at thermal equilibrium

$$\beta = \beta'$$

$$\beta \bar{p} dV = \beta' \bar{p}' dV$$

Then mechanical equilibrium

$$\bar{p} = \bar{p}'$$

Thermodynamics laws and basic statistics relation

Summery of thermodynamic laws

> ➤ Zero law: If two systems are in thermal in equilibrium with a third system, they must be in thermal equilibrium with each other.

> ➤ First law: an equilibrium macrostate of a system can be characterized by a quantity $\bar{E}$ (called internal energy) which has the property that for an isolated $\bar{E}$ =constant. If the system is allowed to interact and thus goes from one macrostate to another, the resulting change in $\bar{E}$ can be written in the form $\Delta \bar{E} = -W + Q$

> ➤ Second law: an equilibrium macrostate of a system can be characterized by a quantity S (called entropy) which has the property that

>> ▪ In any process in which a thermally isolated system goes from one macrostate to another, the entropy tends to increase $\Delta S \geq 0$

>> ▪ If the system is not isolated and under goes a quasi-static infinitesimal process in which it absorbs heat dQ, then $dS = \dfrac{dQ}{T}$

➤ Third law: The entropy S of a system has the limiting property that $T \to 0_{+}$, $S \to S_0$ where

S_0 is a constant independent of all parameters of the particular system

4: Some Application of Statistical and Macroscopic Thermodynamics

Detailed Description of the Activity (Main Theoretical Elements)

Partition function and their properties Ideal gas, validity of classical approximation, equipartition theory, harmonic oscillator at high temperature Distribution of particles Maxwell Boltzmann, Bose Einstein and Fermi-Dirac statistics

Introduction to the Activity

The gas laws described in activity 3 were found by experimental observation, but Boyle's law and Charles' law are not obeyed precisely at all pressures. A gas which obeys the above laws perfectly at all pressures would be a "perfect" or "ideal" gas, and the kinetic theory resulted from an attempt to devise a mechanical model of such a gas based on Newton's laws of motion.

First Law of thermodynamics

$$dQ = dE + dW$$

If the process is quasi-static, the second law gives

$$dQ = TdS$$

The work done by the system when the volume is changed by an amount dV in the process is given by

$$dW = pdV$$

Then the fundamental thermodynamics

$$TdS = dE + pdV$$

The equation of state of an ideal gas

Macroscopically, an ideal gas is described by the equation of state relating its pressure p, volume V, and the absolute temperature T. For v moles of gas, this equation of state is given by

$$pV = vRT$$

The internal energy of an ideal gas depends only on the temperature of the gas, and is independent of the volume

$E = E$ (T) independent of V.

Entropy

The entropy of an ideal gas can readily be computed from the fundamental thermodynamic relation

$$TdS = dE + pdV$$

$$ds = vC_V \frac{dT}{T} + \frac{vR}{V}dV$$

Adiabatic expression or compression

$$pV^\gamma = cons\tan t$$

$$V^{\gamma-1}T = cons$$

Thermodynamic potentials and their relation with thermodynamic variables

The thermodynamic state of a homogeneous system may be represented by means of certain selected variables, such as pressure p, volume v, temperature T, and entropy S. Out of these four variables, any two may vary independently and when known enable the others to be determined. Thus there are only two independent variables and the others may be considered as their function.

The first and the second law of thermodynamics give the four thermodynamic variables

$$dQ = dE + pdV$$ the first law of thermodynamics

$$dQ = TdS$$ the second law of thermodynamics

$$dE = TdS - pdV$$ combined the two laws

Activity

For two independent variables S and V using the fundamental thermodynamics derive the thermodynamics state of a homogeneous system.

Answer

The independent thermodynamic function

$$E = E(S,V)$$ the internal energy

Differentiating the function

$$dE = \left(\frac{\partial E}{\partial S}\right)_V dS + \left(\frac{\partial E}{\partial V}\right)_S dV$$

From the fundamental thermodynamic equation

$$dE = TdS - pdV$$

Comparing the two equations we can get

$$T = \left(\frac{\partial E}{\partial S}\right)_V$$

$$p = -\left(\frac{\partial E}{\partial V}\right)_S$$

Using the second order differential and dE is a perfect differential. E must be independent of the order of differentiation.

$$\left(\frac{\partial}{\partial V}\right)_S \left(\frac{\partial E}{\partial S}\right)_V = \left(\frac{\partial T}{\partial V}\right)_S$$

$$\left(\frac{\partial}{\partial S}\right)_V \left(\frac{\partial E}{\partial V}\right)_S = -\left(\frac{\partial p}{\partial S}\right)_V$$

Then

$$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial p}{\partial S}\right)_V$$

Activity

For two independent variables S and p using the fundamental thermodynamics derive the thermodynamics state of a homogeneous system.

Answer

The independent thermodynamic function

$$dE = TdS - pdV$$

$$dE = TdS - d(pV) + Vdp$$

$$d(E + pV) = TdS + Vdp$$

let $H = E + pV$ which we call it enthalpy

$$H = H(S, p)$$

$$dH = TdS + Vdp$$

Differentiating the function

$$dH = \left(\frac{\partial H}{\partial S}\right)_p dS + \left(\frac{\partial H}{\partial p}\right)_S dp$$

From the thermodynamic equation

$$dH = TdS + Vdp$$

Comparing the two equations we can get

$$T = \left(\frac{\partial H}{\partial S}\right)_p$$

$$V = \left(\frac{\partial H}{\partial p}\right)_S$$

Using the second order differential and dH is a perfect differential. H must be independent of the order of differentiation.

$$\left(\frac{\partial}{\partial p}\right)_S \left(\frac{\partial H}{\partial S}\right)_p = \left(\frac{\partial T}{\partial p}\right)_S$$

$$\left(\frac{\partial}{\partial S}\right)_p \left(\frac{\partial H}{\partial p}\right)_S = \left(\frac{\partial V}{\partial S}\right)_p$$

Then

$$\left(\frac{\partial T}{\partial p}\right)_S = \left(\frac{\partial V}{\partial S}\right)_p$$

Activity

For two independent variables T and V using the fundamental thermodynamics derive the thermodynamics state of a homogeneous system.

Answer

The independent thermodynamic function

$$dE = TdS - pdV$$

$$dE = d(TS) - SdT - pdV$$

$$d(E-TS) = -SdT - pdV$$

let $F = E - TS$ which we call it Helmholtz free energy

$$F = F(T,V)$$

$$dF = -SdT - pdV$$

Differentiating the function $F = F(T,V)$

$$dF = \left(\frac{\partial F}{\partial T}\right)_V dT + \left(\frac{\partial F}{\partial V}\right)_T dV$$

From the thermodynamic equation

$$dF = -SdT - pdV$$

Comparing the two equations we can get

$$S = -\left(\frac{\partial F}{\partial T}\right)_V$$

$$p = -\left(\frac{\partial F}{\partial V}\right)_T$$

Using the second order differential and dH is a perfect differential. H must be independent of the order of differentiation.

$$\left(\frac{\partial}{\partial T}\right)_V \left(\frac{\partial F}{\partial V}\right)_T = -\left(\frac{\partial p}{\partial T}\right)_V$$

$$\left(\frac{\partial}{\partial V}\right)_T \left(\frac{\partial F}{\partial T}\right)_V = -\left(\frac{\partial S}{\partial V}\right)_T$$

Then

$$\left(\frac{\partial p}{\partial T}\right)_V = \left(\frac{\partial S}{\partial V}\right)_T$$

Activity

For two independent variables T and p using the fundamental thermodynamics derive the thermodynamics state of a homogeneous system.

Answer

The independent thermodynamic function

$$dE = TdS - pdV$$

$$dE = d(TS) - SdT - d(pV) + Vdp$$

$$d(E - TS + pV) = -SdT + Vdp$$

let $G = E - TS + pV$ which we call it Gibbs free energy

$$G = G(T, P)$$

$$dG = -SdT + Vdp$$

Differentiating the function $G = G(T, p)$

$$dG = \left(\frac{\partial G}{\partial T} \right)_p dT + \left(\frac{\partial G}{\partial p} \right)_T dp$$

From the thermodynamic equation

$$dG = -SdT + Vdp$$

Comparing the two equations we can get

$$S = -\left(\frac{\partial G}{\partial T} \right)_p$$

$$V = \left(\frac{\partial F}{\partial p} \right)_T$$

Using the second order differential and dH is a perfect differential. H must be independent of the order of differentiation.

$$\left(\frac{\partial}{\partial T} \right)_p \left(\frac{\partial G}{\partial p} \right)_T = \left(\frac{\partial V}{\partial T} \right)_p$$

$$\left(\frac{\partial}{\partial p}\right)_T \left(\frac{\partial G}{\partial T}\right)_p = -\left(\frac{\partial S}{\partial p}\right)_T$$

Then

$$\left(\frac{\partial V}{\partial T}\right)_p = -\left(\frac{\partial S}{\partial p}\right)_T$$

Summary for the thermodynamics function

Maxwell relations

The entire discussion of the preceding section was based upon the fundamental thermodynamics relation

$$dE = TdS - pdV$$

$$\left(\frac{\partial T}{\partial V}\right)_s = -\left(\frac{\partial P}{\partial S}\right)_v$$

$$\left(\frac{\partial T}{\partial p}\right)_s = \left(\frac{\partial V}{\partial S}\right)_p$$

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial p}{\partial T}\right)_v$$

$$\left(\frac{\partial S}{\partial p}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_p$$

Thermodynamics functions

$E..............................E = E(S,V)$
$H \equiv E + pV............H = H(S, p)$
$F \equiv E - TS...............F = F(T,V)$
$G \equiv E - TS + pV......G = G(T, p)$

Next we summarize the thermodynamic relations satisfied by each of these function

$$dE = TdS - pdV$$
$$dH = Tds + Vdp$$
$$dF = -SdT - pdV$$
$$dG = -SdT + Vdp$$

Specific heats

Consider any homogeneous substance whose volume V is the only relevant external parameter.

The heat capacity at constant volume is given by

$$C_V = \left(\frac{dQ}{dT}\right)_V = T\left(\frac{\partial S}{\partial T}\right)_V$$

The heat capacity at constant pressure is similarly given by

$$C_p = \left(\frac{dQ}{dT}\right)_p = T\left(\frac{\partial S}{\partial T}\right)_p$$

Activity

a) For an infinitesimal process of a system the molar specific heat at constant volume and at constant pressure is given by C_V and C_p respectively. Show that $C_p = C_v + R$ which shows

$$C_p > C_v$$

b) Using the heat capacity and thermodynamics function relation show that the heat capacity at constant volume and at constant pressure related by $C_p = C_V - \dfrac{\alpha^2 V}{k}$

Solution for a

At constant volume $dV = 0$

Then first law of thermodynamics reduced to $dQ = dE$

Using the molar heat capacity

$$C_v = \frac{1}{v}\left(\frac{dQ}{dT}\right)_v = \frac{1}{v}\left(\frac{\partial E}{\partial T}\right)_v$$

We have E which is depend on T and independent of V

$$dE = \left(\frac{\partial E}{\partial T}\right)_v dT$$

The change of energy depends only on the temperature change of the gas

$$dE = vC_v dT$$

Substituting in the fundamental equation

$$dQ = vC_v dT + pdV$$

Using the ideal gas equation
$$pV = vRT$$

$$pdV = vRdT$$

The heat absorbed at constant pressure

$$dQ = vC_v dT + vRdT$$

From the definition we have

$$C_p = \frac{1}{v}\left(\frac{dQ}{dT}\right)_p$$

Then

$$\frac{1}{v}\left(\frac{dQ}{dT}\right)_p = C_v + R$$

$C_p = C_v + R$ Which shows $C_p > C_v$

Solution for b

Considering the independent variable $S = S(T, p)$ and second law of thermo dynamics

$$dQ = TdS = T\left[\left(\frac{\partial S}{\partial T}\right)_p dT + \left(\frac{\partial S}{\partial p}\right)_T dp\right] \text{ it is possible to express dp in terms of dT and dV}$$

$$dQ = T\left(\frac{\partial S}{\partial T}\right)_p dT + \left(\frac{\partial S}{\partial p}\right)_T \left[\left(\frac{\partial p}{\partial T}\right)_V dT + \left(\frac{\partial p}{\partial V}\right)_T dV\right] \text{ where at V=constant dV=0}$$

$$dQ = T\left(\frac{\partial S}{\partial T}\right)_p dT + \left(\frac{\partial S}{\partial p}\right)_T \left(\frac{\partial p}{\partial T}\right)_V dT \text{ then}$$

$$\left(\frac{\partial Q}{\partial T}\right)_p = T\left(\frac{\partial S}{\partial T}\right)_p + \left(\frac{\partial S}{\partial p}\right)_T \left(\frac{\partial p}{\partial T}\right)_V$$

$$C_p = C_V + \left(\frac{\partial S}{\partial p}\right)_T \left(\frac{\partial p}{\partial T}\right)_V \text{ from the Maxwell relation } \left(\frac{\partial S}{\partial p}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_p$$

The volume coefficient of expansion of the substance

$$\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p = -\frac{1}{V}\left(\frac{\partial S}{\partial p}\right)_T$$

$$\left(\frac{\partial S}{\partial p}\right)_T = -V\alpha$$

we can express V in terms of T and P

$$dV = \left(\frac{\partial V}{\partial T}\right)_p dT + \left(\frac{\partial V}{\partial p}\right)_T dp = 0 \text{ since V= constant}$$

$$\left(\frac{\partial p}{\partial T}\right)_V = -\frac{\left(\frac{\partial V}{\partial T}\right)_p}{\left(\frac{\partial V}{\partial p}\right)_T}$$

from the isothermal compressibility of the substance

$$k = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T, \quad -kV = \left(\frac{\partial V}{\partial p}\right)_T \quad \left(\frac{\partial S}{\partial p}\right)_T = -V\alpha$$

$$\left(\frac{\partial p}{\partial T}\right)_V = \frac{\alpha}{k} \quad \text{Substituting in the above equation which yields}$$

$$C_p = C_V + \left(\frac{\partial S}{\partial p}\right)_T \left(\frac{\partial p}{\partial T}\right)_V$$

$$= C_V + -V\alpha \frac{\alpha}{k}$$

$$= C_V - \frac{\alpha^2 V}{k}$$

Ensembles system -Canonical distribution

1) Isolated system

An isolated system consists of N number of particles in a specified volume v, the energy of the system being known to lie in some range between E and E + dE. The fundamental statistical postulate asserts that in an equilibrium situation the system is equally likely to be found in any of its accessible states. Thus, if the energy of the system in state r is denoted by E_r, the probability P_r of finding the system in state r is given by

$$P_r = C \qquad \text{If } E < E_r < E + \delta E$$

$$P_r = 0 \qquad \text{Other wise}$$

$$\sum P_r = 1 \qquad \text{Normalized}$$

An ensemble representing an isolated system in equilibrium consists then of system distributed in the above expression. It is some times called a microcanonical ensemble.

2) In contact with reservoir
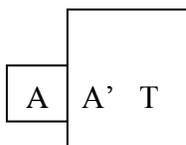
We consider the case of a small system A in thermal interaction with a heat reservoir A'. What is the probability P_r of finding the system A in any one particular microstate r of energy E_r?

The combined system A^0=A+A' and from the conservation of energy E^0=E_r+E'

When A has an energy E_r, the reservoir A' must then have an energy near E'=E^0-E_r.

The number of state $\Omega'(E^0 - E_r)$ accessible to A'

The probability of occurrence in the ensemble of a situation where A in state r is simply proportional the number of state accessible to A^0

$$P_r = C'\Omega'(E')$$

$$\sum_r P_r = 1$$

Using

$$\ln\Omega'(E^0 - E_r) \approx \ln\Omega'(E^0) - \left[\frac{\partial \ln\Omega'}{\partial E'}\right]_{E'=E^0} E_r + ...$$

$$\ln\Omega'(E^0 - E_r) \approx \ln\Omega'(E^0) - \beta E_r$$

$$\Omega'(E') \approx \Omega'(E^0)e^{-\beta E_r}$$

then

$$P_r = C'\Omega'(E^0)e^{-\beta E_r}$$

$$\sum_r P_r = C'\sum_r \Omega'(E^0)e^{-\beta E_r} = 1$$

$$C' = \frac{1}{\sum_r \Omega'(E^0)e^{-\beta E_r}}$$

$$P_r = \frac{e^{-\beta E_r}}{\sum_r e^{-\beta E_r}} \quad \text{The probability of the canonical distribution}$$

Application of canonical ensemble

Activity

Spin system: paramagnetic particles which has N atoms in a system with spin ½

Answer

Considering a system which contains N atoms, spin ½ particles interact with external magnetic field H with the magnetic moment μ

state	Magnetic moment	Energy
+	μ	$E_+ = -\mu H$
−	$-\mu$	$E_- = +\mu H$

The particles has two states + or − the probability

$$P_+ = Ce^{-\beta E_+} = Ce^{\beta \mu H}$$

$$P_- = Ce^{-\beta E_-} = Ce^{-\beta \mu H} \text{ from the normalization condition}$$

P$_+$+P$_-$=1 then we get

$$C = \frac{1}{e^{\beta \mu H} + e^{-\beta \mu H}}$$

$$P_+ = \frac{e^{\beta \mu H}}{e^{\beta \mu H} + e^{-\beta \mu H}}$$

$$P_- = \frac{e^{-\beta \mu H}}{e^{\beta \mu H} + e^{-\beta \mu H}}$$

Molecule in ideal gas

Activity

Consider a monatomic gas at absolute temperature T confined in a container of volume V. The molecule can only be located somewhere inside the container. Derive the canonical distribution for a monatomic non interacting gas

Solution

- The energy of the monatomic gas in a system is given by purely kinetic

$$E = \frac{1}{2}mV^2 = \frac{P^2}{2m}$$

- If the molecule's position lies in the range between r and r+dr and momentum lies between P and P+dP then the volume in phase space is given by $d^3rd^3P = (dxdydz)dp_xdp_ydp_z$)

- The probability that the molecule has position lying in the range between r and r+dr and momentum in the range between p and p+dp

$$P(r,p)d^3rd^3p \propto \left(\frac{d^3rd^3p}{h_0^3}\right)e^{-\beta\frac{p^2}{2m}}$$

- The probability that $P(p)d^3p$ that a molecule has momentum lying in the range between p and p+dp

$$P(p)d^3p = \int_{(r)} P(r,p)d^3rd^3p = Ce^{-\beta\left(\frac{p^2}{2m}\right)}d^3p$$

where we have p=mv $d^3p = md^3v$

Then

$$P'(V) = P(p)d^3p = Ce^{-\beta mV^2/2}$$

Generalized force

Activity

Using the canonical distribution write the generalized force

Solution

If the a system depends on the external parameter x, then $E_r = E_r(x)$ and from the definition of the generalized force we have that

$$X_r = -\frac{\partial E_r}{\partial x}$$

the mean value of the generalized force we can write as

$$\overline{X} = \frac{\sum_r e^{-\beta E_r}\left(-\frac{\partial E_r}{\partial x}\right)}{\sum_r e^{-\beta E_r}}$$

then

$$\overline{X} = \frac{1}{\beta}\frac{\partial \ln Z}{\partial x}$$

the average work done

$$dW = \overline{X}dx$$

where the external parameter is V

$$dW = \frac{1}{\beta}\frac{\partial \ln Z}{\partial V}dV$$

$$\overline{p} = \frac{1}{\beta}\frac{\partial \ln Z}{\partial V}$$

Connection of canonical distribution with thermodynamics

Activity

One can write the thermodynamics function in terms of the partition function derive the equation

Solution

The partition function given by $Z = e^{-\beta E_r(x)}$ so it can be represented in terms of β, x since $E_r = E_r(x)$

Z=Z (β, x) considering a small change

$$d \ln z = \frac{\partial \ln z}{dx}dx + \frac{\partial \ln Z}{\partial \beta}d\beta$$

$d \ln Z = \beta dW - \bar{E} d\beta$

The last term can be written inn terms of the change in $\bar{E}$ rather than the change in β. Thus

$d \ln Z = \beta dW - d(\bar{E}\beta) + \beta d\bar{E}$

$d(\ln Z + \beta\bar{E}) = \beta(dW + d\bar{E}) \equiv \beta dQ$

using the second law of thermodynamics

$dS = \dfrac{dQ}{T}$ therefore

$S \equiv k(\ln Z + \beta\bar{E})$

$TS \equiv kT \ln Z + \bar{E}$

From Helmholtz free energy $F = \bar{E} - TS$

Thus $\ln Z$ is very simply related to Helmholtz free energy F

$F = \bar{E} - TS = -kT \ln Z$

Partition function and their properties

$Z = \sum_r e^{-\beta E_r}$ partition function

If a system can be treated in the classical approximation then its energy $E = E(q_1, \ldots q_n, p_1, \ldots p_n)$ depends on some f generalized coordinates and f momenta.

The partition function in the phase space given by

$Z = \int \ldots \int e^{-\beta E(q_1, \ldots q_n, p_1, \ldots p_n)} \dfrac{dq_1, \ldots dq_n, dp_1, \ldots dp_n}{h^f}$

Activity

Consider the energy of the system is only defined by a function to which is an arbitrary additive constant. If one changes by a constant amount ε_0 the standard state r the energy state becomes

$E^*_r = E_r + \varepsilon_0$ using the partition function

    a. Show the corresponding mean energy shifting by the amount of ε_0

    b. Show the entropy of the combined system will not change $S^* = S$

Solution

a. The mean value of the energy when shifting the system energy by ε_0

Partition function

$$Z^* = \sum_r e^{-\beta(E_r + \varepsilon_0)} \quad = \quad e^{-\beta\varepsilon_0} \sum_r e^{-\beta E_r} = e^{-\beta\varepsilon_0} Z$$

$$\ln Z^* = \ln Z - \beta\varepsilon_0$$

from the definition $\bar{E} = -\dfrac{\partial \ln Z}{\partial \beta}$ and $\bar{E}^* = -\dfrac{\partial \ln Z^*}{\partial \beta}$

$$-\frac{\partial \ln Z^*}{\partial \beta} = -\frac{\partial \ln Z}{\partial \beta} + \varepsilon_0$$

$\bar{E}^* = \bar{E} + \varepsilon_0$ The mean energy also shifted

b. The entropy

let the partition function in terms of the variables $Z^* = Z^*(\beta, x)$

$$d \ln Z^* = \frac{\partial \ln Z^*}{\partial \beta} d\beta + \frac{\partial \ln Z^*}{\partial x} dx \text{ where } \bar{E}^* = -\frac{\partial \ln Z^*}{\partial \beta} \text{ and } \beta dW = \frac{\partial \ln Z^*}{\partial x} dx$$

Then we can find

$$d \ln Z^* = -\bar{E}d\beta + \beta dW$$

using the relation $\bar{E}d\beta = d\left(\beta\bar{E}\right) - \beta d\bar{E}$

$$d \ln Z^* = -d\left(\beta\bar{E}\right) + \beta d\bar{E} + \beta dW$$

$$d \ln Z^* + d\left(\beta\bar{E}\right) = \beta d\bar{E} + \beta dW = \beta \ dQ$$

$$d(\ln Z^* + \beta\bar{E}) = \beta \ dQ = \frac{dQ}{kT}$$

$$S^* = k\left(\ln Z^* + \beta\bar{E}^*\right)$$

Since we can write

$\beta\bar{E}^* = \beta\bar{E} + \beta\varepsilon_0$ and $\ln Z^* = \ln Z - \beta\varepsilon_0$ substituting in the above equation

$$S^* = k\left(\ln Z^* + \beta\bar{E}^*\right) = k\ (\ln Z - \beta\varepsilon_0 + \beta\bar{E} + \beta\varepsilon_0) = k\ (\ln Z + \beta\bar{E}) = S$$

$S^* = S$ the entropy keeping constant

Activity

The second remark concerns the decomposition of partition function for a system A which consists of two parts A' and A'' which interact weakly with each other, if the states of A' and A'' are labelled respectively by r and s find the partition function for the total system

Solution

Part A' state r corresponding energy E_r

Part A'' state s corresponding energy E_s

System A state r,s corresponding energy E_{rs}

The partition function for the system A is given by Z

$$Z = \sum_{r,s} e^{-\beta(E_r + E_s)} \text{ where } E_{r,s} = E_r + E_s$$

then

$$Z = \sum_{r,s} e^{-\beta(E_r + E_s)} = \sum_r e^{-\beta(E_r)} \sum_s e^{-\beta(E_s)}$$

$$Z = Z'Z''$$

$$\ln Z = \ln Z' + \ln Z''$$

Calculation of Thermodynamics quantities with partition function

Activity

Consider a gas consisting of N identical monatomic molecules of mass m enclosed in a container of volume V. The position vector of the ith molecule denoted by r_i

, its momentum by p_i the total energy given by $E = \sum_{i=1}^{N} \frac{P_i^2}{2m} + U(r_1, r_2, ... r_N)$ where for non-interacting

monatomic ideal gas U=0 and write the partition function in phase space

Solution

Taking a gas consisting of N identical monatomic molecules of mass m enclosed in a container of volume V. The position vector of the ith molecule denoted by r_i

, its momentum by p_i the total energy given by $E = \sum_{i=1}^{N} \frac{P_i^2}{2m} + U(r_1, r_2, ... r_N)$ where for non-interacting

monatomic ideal gas U=0 therefore the partition function in phase space can be given as follows

$$Z = \int \exp\left\{ -\beta\left[\frac{1}{2m}\left(p_1^2 + ... + p_N^2 \right) + U(r_1, ... r_N) \right] \right\} \frac{d^3 r_1 ... d^3 r_N \, dp_1^3 ... dp_N^3}{h_0^{3N}}$$

$$Z = \frac{1}{h_0^{3N}} \int \exp\left\{ -\beta\left[\frac{1}{2m}\left(p_1^2 + ... + p_N^2 \right) \right] \right\} dp_1^3 ... dp_N^3 \int \exp\left\{ -\beta\left[U(r_1, ... r_N) \right] \right\} d^3_1 ... d^3_N$$

$$\int \exp\left\{ -\beta\left[U(r_1, ... r_N) \right] \right\} d^3_1 ... d^3_N = V^N$$

$$Z = \frac{V^N}{h_0^{3N}} \int \exp\left\{ -\beta\left[\frac{1}{2m}\left(p_1^2 + ... + p_N^2 \right) \right] \right\} dp_1^3 ... dp_N^3$$

where $p^2_1 = P_{1x}^2 + p_{1y}^2 + p_{1z}^2$, $dp_1^3 = dp_{1x} dp_{1y} dp_{1z}$ so for the ith particle

$$\xi = \frac{V}{h_0^{\,3}} \int \exp\left\{ -\beta\left[\frac{1}{2m}\left(p^2\right) \right]\right\} dp$$

$$Z = \xi^N$$

$$\int_{-\infty}^{\infty} e^{\frac{-\beta p_{1x}^{\,2}}{2m}}\, dp_{1x} = \sqrt{\frac{2m\pi}{\beta}} \;,\;\; \int_{-\infty}^{\infty} e^{\frac{-\beta p^2}{2m}}\, dp = \left(\frac{2m\pi}{\beta}\right)^{\!\frac{3}{2}}$$

$$\xi = \frac{V}{h_0^{\,3}} \left(\frac{2m\pi}{\beta}\right)^{\!\frac{3}{2}} = V\left(\frac{2m\pi}{\beta h_0^{\,2}}\right)^{\!\frac{3}{2}}$$

$$Z = \xi^N = \left[V\left(\frac{2m\pi}{\beta h_0^{\,2}}\right)^{\!\frac{3}{2}} \right]^{N}$$ the thermodynamics quantities with the partition function

Taking the logarithm

$$\ln Z = N\left\{ \ln V + \frac{3}{2}\ln\left(\frac{2m\pi}{h_0^{\,2}}\right) - \frac{3}{2}\ln\beta \right\}$$

Activity

With the given partition function, find

i) The value for the mean pressure,

ii) The mean energy,

iii) The heat capacity,

iV) The entropy

Solution

i) The mean pressure

$$\bar{p} = \frac{1}{\beta}\frac{\partial \ln Z}{\partial V} = \frac{NkT}{V}$$

$$\bar{p}V = NkT$$

ii) The total mean energy

$$\bar{E} = -\frac{\partial \ln Z}{\partial \beta}$$

$$\bar{E} = \frac{3}{2}\frac{N}{\beta} = \frac{3}{2}NkT$$

$$\bar{\varepsilon} = \frac{3}{2}kT$$

$$\bar{E} = N\bar{\varepsilon}$$

iii) The heat capacity at constant volume

$$C_V = \left(\frac{\partial \bar{E}}{\partial T}\right)_V = \frac{3}{2}R$$

iV)The entropy

$$S \equiv k\left(\ln Z + \beta \bar{E}\right), \text{ where}$$

$$\beta \bar{E} = \frac{3}{2}N$$

$$\ln Z = N\left\{\ln V + \frac{3}{2}\ln\left(\frac{2m\pi}{h^2_0}\right) - \frac{3}{2}\ln \beta\right\}$$

$$S = Nk\left\{\ln V + \frac{3}{2}\ln\left(\frac{2m\pi}{h^2_0}\right) - \frac{3}{2}\ln \beta + \frac{3}{2}\right\}$$

$$S = Nk\left\{\ln V + \frac{3}{2}\ln T + \frac{3}{2}\left(\ln\left(\frac{2m\pi k}{h^2_0}\right) + 1\right)\right\} \text{ where } \delta = \frac{3}{2}\left\{\ln\left(\frac{2m\pi k}{h^2_0}\right) + 1\right\}$$

$$S = Nk\left\{\ln V + \frac{3}{2}\ln T + \delta\right\}$$

Then the Mean Energy

$$\bar{\varepsilon}_i = \frac{\int e^{-\beta(\varepsilon_i+E')}\varepsilon_i dp_1,...dp_f}{\int e^{-\beta(\varepsilon_i+E')}dp_1,...dp_f}$$

$$\bar{\varepsilon}_i = \frac{\int e^{-\beta\varepsilon_i}\varepsilon_i dp_i \int e^{-\beta E'}dp_1,...dp_f}{\int e^{-\beta\varepsilon_i}dp_i \int e^{-\beta E'}dp_1,...dp_f}$$

$$\bar{\varepsilon}_i = \frac{\int e^{-\beta\varepsilon_i}\varepsilon_i dp_i}{\int e^{-\beta\varepsilon_i}dp_i} \quad \text{considering that} \quad \varepsilon_i = \frac{p^2}{2m} = bp^2 \text{ then}$$

$$\bar{\varepsilon}_i = -\frac{\partial}{\partial\beta}\ln\int e^{-\beta\frac{p_i^2}{2m_i}}dp_i \text{ let}$$

$$\bar{\varepsilon}_i = -\frac{\partial}{\partial\beta}\ln\sqrt{\frac{4\pi m_i}{\beta}}$$

$$\bar{\varepsilon}_i = \frac{kT}{2}$$

The Harmonic Oscillator at high thermal energy

Summery of harmonic oscillator

For a1D-harmonic oscillator which is in equilibrium with a heat reservoir at absolute temperature T.

> $E = \frac{P^2}{2m} + \frac{1}{2}kx^2$ the energy of the oscillator

> $E = \left(n + \frac{1}{2}\right)\hbar\omega$

Is the energy of the oscillator in quantum mechanics the angular frequency $\omega = \sqrt{\dfrac{k}{m}}$

Activity

Using the partition function of the harmonic oscillator derive the mean energy of the oscillator for $\beta\hbar\omega \ll 1$ and $\beta\hbar\omega \gg 1$

Solution

The mean energy for the harmonic oscillator given by

$$\bar{E} = \frac{\displaystyle\sum_{n=0}^{\infty} e^{-\beta E_n} E_n}{\displaystyle\sum_{n=0}^{\infty} e^{-\beta E_n}}$$

$$\bar{E} = -\frac{\partial \ln Z}{\partial \beta}$$

where

$$Z = \sum_{n=0}^{\infty} e^{-\beta E_n} = \sum_{n=0}^{\infty} e^{-\beta\left(n+\frac{1}{2}\right)\hbar\omega}$$

$$Z = e^{-\beta\frac{\hbar\omega}{2}} \sum_{n=0}^{\infty} e^{-\beta n\hbar\omega}$$

$$Z = e^{-\beta\frac{\hbar\omega}{2}} \left(1 + e^{-\beta\hbar\omega} + e^{-2\beta\hbar\omega} \ldots\right)$$

$$Z = e^{-\beta\frac{\hbar\omega}{2}} \left(1 - e^{-\beta\hbar\omega}\right)^{-1}$$

$$\bar{E} = -\frac{\partial}{\partial\beta}\ln\left[e^{-\beta\frac{\hbar\omega}{2}}\left(1-e^{-\beta\hbar\omega}\right)^{-1}\right]$$

$$\bar{E} = -\frac{\partial}{\partial\beta}\left[\ln(e^{-\beta\frac{\hbar\omega}{2}})-\ln\left(1-e^{-\beta\hbar\omega}\right)\right]$$

$$\bar{E} = \frac{\hbar\omega}{2}+\frac{e^{-\beta\hbar\omega}\hbar\omega}{1-e^{-\beta\hbar\omega}}$$

i) Considering the case $\beta\hbar\omega \ll 1$

From the Taylor expansion

$$e^{\beta\hbar\omega} = 1+\beta\hbar\omega+\frac{1}{2}(\beta\hbar\omega)^2+... \quad \text{neglecting the higher order since } \beta\hbar\omega \ll 1$$

substituting in the equation

$$\bar{E} = \hbar\omega\left(\frac{1}{2}+\frac{1}{e^{\beta\hbar\omega}-1}\right)$$

$$\bar{E} \approx \hbar\omega\left(\frac{1}{2}+\frac{1}{\beta\hbar\omega}\right)$$

$$\beta\hbar\omega \ll 1, \quad \frac{1}{2}+\frac{1}{\beta\hbar\omega}\approx\frac{1}{\beta\hbar\omega}$$

$$\bar{E} \approx \frac{1}{\beta}=kT$$

ii) Considering $\beta\hbar\omega \gg 1$

then $\bar{E} = \hbar\omega\left(\dfrac{1}{2}+\dfrac{1}{e^{\beta\hbar\omega}-1}\right)$

$$\bar{E} \approx \hbar\omega\left(\frac{1}{2} + e^{-\beta\hbar\omega}\right)$$ which shows $T \to 0$ the ground state energy given by

$$\bar{E} = \frac{1}{2}\hbar\omega$$

Kinetic theory of dilute gasses in equilibrium

Maxwell velocity distribution

Summery for Maxwell velocity distribution

Consider a molecule of mass m in a dilute gas the energy ε of the molecule is equal to

$$\varepsilon = \frac{P^2}{2m} + \varepsilon^{int}$$

$\dfrac{P^2}{2m}$ due to the kinetic energy of the centre of mass motion

ε^{int} the molecule is not monatomic the internal energy due to rotation and vibration of the atom with respect to the molecular centre of mass

The probability $P_s(r,p)d^3rd^3p$ of finding the molecule with centre-of –mass variables in the

ranges (r,dr) and (p,dp) and with internal state specified by s the result

$$P_s(r,p)d^3rd^3p \propto e^{-\beta\left(\frac{p^2}{2m} + \varepsilon^{int}\right)}d^3rd^3p$$

where $e^{-\beta\varepsilon^{int}}$ contributes for the constant proportionality

$$P_s(r,p)d^3rd^3p \propto e^{-\beta\frac{p^2}{2m}}d^3rd^3p$$

$$f(r,V)d^3rd^3V = Ce^{-\beta\frac{V^2}{2m}}d^3rd^3V$$

Activity

Using the normalization condition for N number of molecules in a system derive the value of C and write the Maxwell velocity distribution

Solution

$$\iint_{r\ V} f(r,V)d^3rd^3V = N$$

$$\iint_{r\ V} Ce^{-\beta\frac{V^2}{2m}}d^3rd^3V = N$$

$$C\int_r d^3r \left(\int_{-\infty}^{\infty} e^{-\beta\frac{mV^2_x}{2m}} dV_x \right)^3 = N$$

$$CV\left[\sqrt{\frac{2\pi}{\beta m}} \right]^3 = N$$

$$C = \frac{N}{V}\left[\frac{\beta m}{2\pi} \right]^{\frac{3}{2}}, n = \frac{N}{V} \text{ total number of molecule per unit volume}$$

$$f(r,V)d^3rd^3V = n\left(\frac{\beta m}{2\pi} \right)^{\frac{3}{2}} e^{-\beta\frac{V^2}{2m}}d^3rd^3V \quad \text{Maxwell velocity distribution}$$

Activity

Derive the velocity distribution component

Solution

Let the number of molecule per unit volume with x-component of velocity in the range between V_x and V_x+dV_x, irrespective of the values of their other velocity is given by

$$g(V_x)dV_x = \int_{V_x} \int_{V_y} f(V)d^3V$$

$$g(V_x)dV_x = n\left(\frac{m}{2\pi kT} \right)^{\frac{3}{2}} \int_{V_y} e^{-\left(\frac{m}{2kT}\right)V^2_y} dV_y \int_{V_z} e^{-\left(\frac{m}{2kT}\right)V^2_z} d^3V_z$$

$$g(V_x)dV_x = n\left(\frac{m}{2\pi kT} \right)^{\frac{3}{2}} e^{-\left(\frac{m}{2kT}\right)V^2_x} \int_{-\infty}^{\infty} e^{-\left(\frac{m}{2kT}\right)V^2_y} dV_y \int_{-\infty}^{\infty} e^{-\left(\frac{m}{2kT}\right)V^2_z} dV_z$$

$$g(V_x)dV_x = n\left(\frac{m}{2\pi kT}\right)^{3/2}\left(\frac{m}{2kT}\right)^{-1} e^{-\left(m/2kT\right)V_x^2} dV_x$$

The graph $g(V_x)$ versus V_x

Problem

Solve the value for

$\bar{V}_x$ and $\overline{V_x^2}$

particles in state r by ε_r
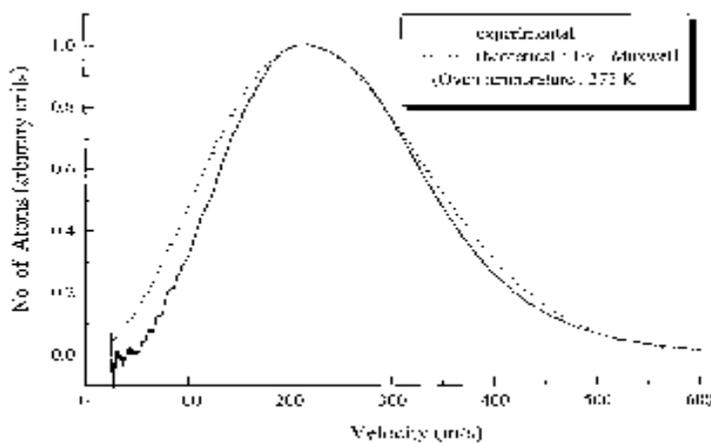
Formulation of the statistical Problems

Consider a gas of identical particles in a volume V in equilibrium at the temperature T. We shall use the following notation

➢ Label the possible quantum states of a single particle by r or s

➢ Denote the energy of

➢ Denote the number of particles in state r by n_r

➢ Label the possible quantum states of the whole gas by R

The total energy of the gas when it is in some state R where there are n_1 particle r=1, n_2 particles in state r=2 etc.,

$$E_R = n_1\varepsilon_1 + n_2\varepsilon_2 + \dots = \sum_r n_r\varepsilon_r$$

The total number of the gas N is given by $\sum_r n_r = N$

In order to calculate the thermodynamic function of the gas it is necessary to calculate its partition function

$$Z = \sum_R e^{-\beta E_R}$$

$$Z = \sum_R e^{-\beta(n_1\varepsilon_1 + n_2\varepsilon_2 + \dots)}$$

Activity

Derive the mean number of the particles in state s

Solution

$$\bar{n}_s = \frac{\sum_R n_s e^{-\beta(n_1\varepsilon_1 + n_2\varepsilon_2 + \dots)}}{\sum_R e^{-\beta(n_1\varepsilon_1 + n_2\varepsilon_2 + \dots)}}$$

$$\bar{n}_s = -\frac{1}{\beta}\frac{\partial \ln Z}{\partial \varepsilon_s}$$

Problem

Calculate the dispersion

Solution

One can similarly write down an expression for the dispersion of the number of particles in state s. One can use the general relation.

$$\overline{(\Delta n_s)^2} = \overline{(n_s - \bar{n}_s)^2} = \overline{n_s^2} - \bar{n}_s^2$$

For the case $\overline{n_s^2}$

$$\overline{n_s^2} = \frac{\sum\limits_R n_s^2 e^{-\beta(n_1\varepsilon_1+n_2\varepsilon_2+...)}}{\sum\limits_R e^{-\beta(n_1\varepsilon_1+n_2\varepsilon_2+...)}}$$

$$\overline{n_s^2} = -\frac{1}{\beta^2 Z}\frac{\partial^2 \ln Z}{\partial\varepsilon_s^2}$$

$$\overline{n_s^2} = \frac{1}{\beta^2}\left[\frac{\partial}{\partial\varepsilon_s}\left(\frac{1}{Z}\frac{\partial Z}{\partial\varepsilon_s}\right)+\frac{1}{Z^2}\left(\frac{\partial Z}{\partial\varepsilon_s}\right)^2\right]$$

$$\overline{n_s^2} = \frac{1}{\beta^2}\left[\frac{\partial}{\partial\varepsilon_s}\left(\frac{1}{Z}\frac{\partial Z}{\partial\varepsilon_s}\right)+\beta^2\overline{n_s}^2\right]$$

$$\overline{(\Delta n_s)^2} = \frac{1}{\beta^2}\left[\frac{\partial}{\partial\varepsilon_s}\left(\frac{1}{Z}\frac{\partial Z}{\partial\varepsilon_s}\right)\right]$$

$$= \frac{1}{\beta^2}\frac{\partial^2 \ln Z}{\partial\varepsilon_s^2}$$

$$\overline{(\Delta n_s)^2} = -\frac{1}{\beta}\frac{\partial\overline{n_s}}{\partial\varepsilon_s}\quad \text{the dispersion of the distribution of particles}$$

Photon Statistics

The average numbers of particles in state s in case of photon statistics

$$\overline{n_s} = \frac{\sum n_s e^{-\beta n_s\varepsilon_s}}{\sum e^{-\beta n_s\varepsilon_s}}$$

$$\overline{n_s} = \frac{-\frac{1}{\beta}\frac{\partial}{\partial\varepsilon_s}\sum e^{-\beta n_s\varepsilon_s}}{\sum e^{-\beta n_s\varepsilon_s}}$$

$$\bar{n}_s = -\frac{1}{\beta}\frac{\partial}{\partial \varepsilon_s}\ln\sum e^{-\beta n_s \varepsilon_s} \quad \text{Using the geometric series}$$

$$\sum_{n_s=0}^{\infty} e^{-\beta n_s \varepsilon_s} = 1 + e^{-\beta \varepsilon_s} + e^{-2\beta \varepsilon_s} + \ldots = \frac{1}{1-e^{-\beta \varepsilon_s}}$$

$$\bar{n}_s = -\frac{1}{\beta}\frac{\partial}{\partial \varepsilon_s}\ln\frac{1}{1-e^{-\beta \varepsilon_s}}$$

$$\bar{n}_s = \frac{1}{\beta}\frac{\partial}{\partial \varepsilon_s}\ln\left(1-e^{-\beta \varepsilon_s}\right)$$

$$\bar{n}_s = \frac{1}{e^{-\beta \varepsilon_s}-1} \quad \text{The average number of particles in Plank's distribution}$$

Fermi-Dirac Statistics

Activities

Consider particles in a system where the total number N of particles is fixed $n_1, n_{2,\ldots}$ such that

$n_r = 0$ and $n_r = 1$ for each r, but these numbers must always satisfy $\sum_r n_r = N$, let us derive the

average number of particles in a given system

Solution

Considering the above mentioned condition where the total number N of particles is fixed

$n_1, n_{2,\ldots}$ such that $n_r = 0$ and $n_r = 1$ for each r, but these numbers must always satisfy $\sum_r n_r = N$, to

derive the average number of particles in a given system for Fermi-Dirac Statistics we consider

the partition function

$$z_s(N) = \sum_{n_1, n_{2,\ldots}}^{(s)} e^{-\beta(n_1 \varepsilon_1 + n_2 \varepsilon_2 + \ldots)} \quad \text{then}$$

$$\sum_{r}{}^{(s)}n_r = N \quad \text{s state omitted}$$

$$\bar{n}_s = \frac{\sum\limits_{n_s} n_s e^{-\beta n_s \varepsilon_s} \sum\limits_{n_1,n_2,\ldots}{}^{(s)} e^{-\beta(n_1\varepsilon_1 + n_2\varepsilon_2 + \ldots)}}{\sum\limits_{n_s} e^{-\beta n_s \varepsilon_s} \sum\limits_{n_1,n_2,\ldots}{}^{(s)} e^{-\beta(n_1\varepsilon_1 + n_2\varepsilon_2 + \ldots)}}$$

since $n_s = 0$ and 1

$$\bar{n}_s = \frac{0 + e^{-\beta\varepsilon_s}\sum\limits_{n_1,n_2,\ldots}{}^{(s)} e^{-\beta(n_1\varepsilon_1 + n_2\varepsilon_2 + \ldots)}}{\sum\limits_{n_1,n_2,\ldots}{}^{(s)} e^{-\beta(n_1\varepsilon_1 + n_2\varepsilon_2 + \ldots)} + e^{-\beta\varepsilon_s}\sum\limits_{n_1,n_2}{}^{(s)} e^{-\beta(n_1\varepsilon_1 + n_2\varepsilon_2 + \ldots)}}$$

$$\bar{n}_s = \frac{0 + e^{-\beta\varepsilon_s} Z_s(N-1)}{Z_s(N) + e^{-\beta\varepsilon_s} Z_s(N-1)} \quad \text{taking the ratio of the equation}$$

$$\bar{n}_s = \frac{1}{\left[\dfrac{Z_s(N)}{Z_s(N-1)}\right] e^{\beta\varepsilon_s} + 1}$$

taking the Taylor expansion of $\ln Z_s(N - \Delta N)$ for $\Delta N \ll N$

$$\ln Z_s(N - \Delta N) = \ln Z_s(N) - \frac{\partial \ln Z_s(Z)}{\partial N} \Delta N$$

$$\ln\left(\frac{Z_s(N-1)}{Z_s(N)}\right) = -\alpha \Delta N \quad \text{where} \quad \alpha = \frac{\partial \ln Z_s(N)}{\partial N}$$

$$Z_s(N - \Delta N) = Z_s(N) e^{-\alpha \Delta N} \quad \text{if we approximate} \quad \Delta N \approx 1$$

$$Z_s(N-1) = Z_s(N) e^{-\alpha}$$

since we have

$$\bar{n}_s = \frac{1}{\left[Z_s(N) \Big/ Z_s(N-1) \right] e^{\beta \varepsilon_s} + 1} \quad \text{and substituting}$$

$$\bar{n}_s = \frac{1}{e^{\alpha + \beta \varepsilon_s} + 1} \quad \text{which is Fermi-Dirac Distribution}$$

Bose-Einstein Statistics

Activity

Derive the distribution of the particles in a system considering the case where the total number N of particles is fixed $n_1, n_{2,...}$ such that $n_r = 0,1,2,....$but these numbers must always satisfy $\sum_r n_r = N$

Solution

$$z_s(N) = \sum_{n_1, n_{2,...}}^{(s)} e^{-\beta(n_1 \varepsilon_1 + n_2 \varepsilon_2 + ...)}$$

$$\bar{n}_s = \frac{\sum_{n_s} n_s e^{-\beta n_s \varepsilon_s} \sum_{n_1, n_2,...}^{(s)} e^{-\beta(n_1 \varepsilon_1 + n_2 \varepsilon_2 + ...)}}{\sum_{n_s} e^{-\beta n_s \varepsilon_s} \sum_{n_1, n_2,...}^{(s)} e^{-\beta(n_1 \varepsilon_1 + n_2 \varepsilon_2 + ...)}}$$

$$\bar{n}_s = \frac{0 + e^{-\beta \varepsilon_s} Z_s(N-1) + 2e^{-2\beta \varepsilon_s} Z_s(N-2) + ...}{Z_s(N) + e^{-\beta \varepsilon_s} Z_s(N-1) + e^{-2\beta \varepsilon_s} Z_s(N-2) + ...}$$

where

$$Z_s(N-1) = Z_s(N) e^{-\alpha} \quad \text{and}$$

$$Z_s(N-2) = Z_s(N) e^{-2\alpha}$$

$$\bar{n}_s = \frac{Z_s(N)\left(0 + e^{-\beta \varepsilon_s} e^{-\alpha} + 2e^{-2\beta \varepsilon_s} e^{-2\alpha} + ...\right)}{Z_s(N)\left(1 + e^{-\beta \varepsilon_s} e^{-\alpha} + e^{-2\beta \varepsilon_s} e^{-2\alpha} + ...\right)}$$

$$\bar{n}_s = \frac{\left(0 + e^{-\beta \varepsilon_s} e^{-\alpha} + 2e^{-2\beta \varepsilon_s} e^{-2\alpha} + ...\right)}{\left(1 + e^{-\beta \varepsilon_s} e^{-\alpha} + e^{-2\beta \varepsilon_s} e^{-2\alpha} + ...\right)}$$

$$\bar{n}_s = \frac{\sum n_s e^{-(\alpha + \beta \varepsilon_s)n_s}}{\sum e^{-(\beta \varepsilon_s + \alpha)n_s}}$$

considering

$$\sum n_s e^{-(\beta \varepsilon_s + \alpha)n_s} = -\frac{\partial}{\partial \alpha} \sum e^{-(\beta \varepsilon_s + \alpha)n_s}$$

$$\bar{n}_s = \frac{\sum n_s e^{-(\alpha + \beta \varepsilon_s)n_s}}{\sum e^{-(\beta \varepsilon_s + \alpha)n_s}} = -\frac{\partial}{\partial \alpha} \ln \sum_{n_s=0}^{\infty} e^{-(\beta \varepsilon_s + \alpha)n_s}$$

taking the expansion

$$\sum_{n_s=0}^{\infty} e^{-(\beta \varepsilon_s + \alpha)n_s} = 1 + e^{-(\beta \varepsilon_s + \alpha)} + e^{-2(\beta \varepsilon_s + \alpha)} + ... = \left(1 - e^{-(\beta \varepsilon_s + \alpha)}\right)^{-1}$$

$$\sum_{n_s=0}^{\infty} e^{-(\beta \varepsilon_s + \alpha)n_s} = \left(1 - e^{-(\beta \varepsilon_s + \alpha)}\right)^{-1}$$

$$n_s = -\frac{\partial}{\partial \alpha} \ln \left(1 - e^{-(\beta \varepsilon_s + \alpha)}\right)^{-1}$$

$$= \frac{e^{-(\beta \varepsilon_s + \alpha)}}{1 - e^{-(\beta \varepsilon_s + \alpha)}}$$

$$= \frac{1}{e^{(\beta \varepsilon_s + \alpha)} - 1} \quad \text{Bose-Einstein Distribution}$$

Maxwell-Boltzmann statistics

Activity

With the help of the partition function is $z = \sum_{R} e^{-\beta(n_1 \varepsilon_1 + n_2 \varepsilon_2 + ...)}$ compute the Maxwell-Boltzmann

distribution distribution

Solution

Hence, the partition function is $z = \sum_R e^{-\beta(n_1 \varepsilon_1 + n_2 \varepsilon_2 + ...)}$

For N number of molecules there are, for given values of $(n_1, n_2, ...)$

$\dfrac{N!}{n_1! n_2! ..}$ possible ways in which the particle can be put into the given single- particle states, so that

there are n_1 particles in state 1, n_2 particles in state 2, etc. By virtue of the distinguishability of particles, each of these possible arrangements corresponds then to a distinct state for the whole gas. Hence the partition function can be written

$$z = \sum_{n_1, n_2, ...} \frac{N!}{n_1! n_2! ...} e^{-\beta(n_1 \varepsilon_1 + n_2 \varepsilon_2 + ...)}$$

where the sum overall values $n_r = 0, 1, 2, ...$ for each r, subject to the restriction $\sum_r n_r = N$

$$z = \sum_{n_1, n_2, ...} \frac{N!}{n_1! n_2! ...} e^{-(\beta \varepsilon_1) n_1} e^{-(\beta \varepsilon_2) n_2 ...}$$

expanding the polynomial

$$z = \sum_{n_1, n_2, ...} \frac{N!}{n_1! n_2! ...} e^{-(\beta \varepsilon_1) n_1} e^{-(\beta \varepsilon_2) n_2 ...} = \left(e^{-\beta \varepsilon_1} + e^{-\beta \varepsilon_2} + ... \right)^N$$

$$\ln Z = N \ln \left(\sum_r e^{-\beta \varepsilon_r} \right)$$

from the mean values of the distribution of the particle we have defined as

$$\bar{n}_s = -\frac{1}{\beta} \frac{\partial \ln Z}{\partial \varepsilon_s} = -\frac{1}{\beta} N \frac{-\beta e^{-\beta \varepsilon_s}}{\sum_r e^{-\beta \varepsilon_r}} \qquad \text{where} \qquad \sum_r e^{-\beta \varepsilon_r} = e^{-\beta \varepsilon_s} \sum_{r=1}^{s} e^{-\beta \varepsilon_r}$$

$$\bar{n}_s = N \frac{e^{-\beta \varepsilon_s}}{\sum_r e^{-\beta \varepsilon_r}} \quad \text{this is called the Maxwell-Boltzmann distribution}$$