Statistical Mechanics

by

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Unit:-

Classical Theory of Radiation

Topic- 10. Saha’s Ionization Formula

Saha Ionisation Equation

Ionisation energies of atoms are of the order of tens of eV (for hydrogen, it is 13.6 eV). The equivalent temperature is $\sim 10^4 - 10^5$ K. Such high temperatures are easily realised in various astrophysical situations (stars, in particular). Hence, it is of importance to astrophysical studies. Thermodynamically, ionisation can be looked upon as a chemical reaction where one reactant transforms into two new ones (or vice-versa). Such a treatment was first developed by Meghnad Saha, and the essence is captured in the famous ***Saha Ionisation equation***.

In general, a process that can change the number of particles of a certain kind, is called a chemical reaction. A generic reaction is written as,

$$\sum_j R_j \alpha_j = 0, \tag{105}$$

where, R_j and α_j are the chemical symbol and the no. of particles of species j taking part in the reaction. Since, reactions take place in equilibrium with their surroundings, temperature and pressure remain constant, same as that of the surroundings. The appropriate thermodynamics potential for the overall system is then the Gibb's potential with the equilibrium condition given by,

$$dG = -S\,dT + VdP = 0\,. \tag{106}$$

(It is, of course, conceivable to have reactions taking place under different circumstances. An appropriate thermodynamic potential need to be used to describe such reactions.) Now, for each particle species we have,

$$dG_j = \mu_j\,dN_j, \quad \text{with} \quad dT,\, dP = 0\,, \tag{107}$$

which, in equilibrium, implies,

$$dG = \sum_j dG_j = \sum_j \mu_j dN_j = 0\,. \tag{108}$$

However, the number of particles, of a particular species, would change strictly according to the specific reaction being considered. Each time the reaction happens, the number of each reactant R_j changes only by n_j. Thus, the total change, dN_j must be proportional to α_j. At equilibrium then, the chemical potentials of different reactants satisfy the relation

$$\sum_j \mu_j\,\alpha_j = 0, \tag{109}$$

which is the law of chemical equilibrium. It should be remembered that we need to use the total chemical potential (inclusive of the rest mass of the particle) here. Because, this condition implies that

$$\sum_j \mu_j^{NR}\,\alpha_j = 0, \tag{110}$$

only if $\sum_j m_j\,\alpha_j = 0$, i.e., the total rest mass is invariant through the reaction in consideration ($\mu^{NR} = \mu - mc^2$). Since, that is not true of all reactions (notably, the fusion reactions in stars) it is not appropriate to use μ^{NR} in general.

Let us now suppose that the reactants can be treated as classical ideal gases. The single particle partition function for an ideal gas is given by,

$$Q_1 = V\left(\frac{mk_BT}{2\pi\hbar^2}\right)^{3/2} = \frac{V}{\Lambda_T}, \tag{111}$$

where Λ_T can be thought of as the thermal de Broglie volume associated with a particle. Then the partition function for an N-particle idea gas is,

$$Q = \frac{1}{N!}\left(\frac{V}{\Lambda_T}\right)^N, \tag{112}$$

and the grand partition function is

$$\mathcal{Z} = \sum_{N=0} e^{\beta\mu N}\frac{Q^N}{N!}. \tag{113}$$

Now,

$$\begin{aligned} P &= k_BT\frac{\partial \ln \mathcal{Z}}{\partial V}|_{T,\mu} \\ &= \frac{e^{\beta\mu}}{\beta\Lambda_T}. \end{aligned} \tag{114}$$

Using the ideal gas equation of state $PV = Nk_BT = N/\beta$ we find

$$n = \frac{N}{V} = \frac{e^{\beta\mu}}{\Lambda_T}. \tag{115}$$

If the particles of the reactants (assumed to behave like classical, ideal gases) have internal degrees of freedom, this formula is modified to

$$n = \frac{qe^{\beta\mu}}{\Lambda_T}, \tag{116}$$

where q is the contribution to the partition function due to the internal degrees of freedom, implying

$$\mu = \frac{1}{\beta}\ln\left(\frac{n\Lambda_T}{q}\right). \tag{117}$$

Using this in the equation for chemical equilibrium we have,

$$\sum_j \alpha_j \ln\left(\frac{n_j\Lambda_j}{q_j}\right) = 0, \;\Rightarrow\; \Pi_j n_j^{\alpha_j} = \Pi_j\left(\frac{q_j}{\Lambda_j}\right)^{\alpha_j}. \tag{118}$$

Here Λ_j is the quantum volume for the j-th species. The contribution of the internal degrees of freedom to the partition function can be written as

$$q = q^0 e^{-\beta\epsilon^0}, \tag{119}$$

where ϵ^0 is the energy of the ground state of the internal degrees of freedom and q^0 is the internal partition funtion for zero ground state energy. If there are only one kind of particles, then one can set $\epsilon^0 = 0$, but it can not be done when different species of particles are involved and we have

$$\Pi_j n_j^{\alpha_j} = \Pi_j \left(\frac{q_j^0 e^{-\beta \epsilon_j^0}}{\Lambda_j} \right)^{\alpha_j} . \tag{120}$$

For example, consider

$$X + Y \rightleftarrows XY \tag{121}$$

where X and Y denote two kinds of particles and XY denote their bound state. Then in equilibrium, the number densities of X, Y and XY are governed by,

$$\frac{n_X n_Y}{n_{XY}} = \frac{q_X^0 q_Y^0}{q_{XY}^0} \frac{\Lambda_{XY}}{\Lambda_X \Lambda_Y} exp \left[\beta(\epsilon_{XY}^0 - \epsilon_X^0 - \epsilon_Y^0) \right] . \tag{122}$$

The quantity multiplying β in the exponent is the binding energy of the molecule XY if the atoms X and Y react to form it.

Ionisation : Consider an ionisation equation of the following form

$$X^+ + e^- \rightleftarrows X , \tag{123}$$

where X can be looked upon as the bound state of the ion X^+ and the electron. As the masses of the ion and the atom are almost equal we have $\Lambda_{X^+} \simeq \Lambda_X$. Therefore,

$$\frac{n_{X^+} n_{e^-}}{n_X} = \frac{q_{X^+}^0 q_{e^-}^0}{q_X^0} \frac{e^{-\beta\epsilon}}{\Lambda_e} . \tag{124}$$

The first factor on the right hand side usually contains the degeneracy factors due to spin etc. If we define the fraction of the particles in the following manner,

$$n_X + n_{X^+} = n_t, \ f = \frac{n_{x^+}}{n_t}, \tag{125}$$

then, with charge neutrality ($n_{X^+} = n_e$)

$$\frac{f^2}{1 - f} = \frac{q_{X^+}^0 q_{e^-}^0}{q_X^0} \frac{e^{-\beta\epsilon}}{n_t \Lambda_e} . \tag{126}$$

This is the ***Saha Ionisation Equation***. In the NR limit $\Lambda \propto T^{-3/2}$, so at high temperatures, the right hand side becomes very large. This means at high temperatures the ionisation fraction is very large. As $T \to 0$, we have $f \to 0$ although the validity of this equation should be suspect in this limit because the gases may not behave as classical ideal gases.

Problem set up Unit-III

1 Classical Statistics

1.1 Macrostate and Microstate, Phase Space, Ensemble, Thermodynamic Probability

Problem 1: Consider a particle undergoing simple harmonic motion such that the position of the particle changes with time as $x = x_0 \cos(\omega t + \phi)$, where the phase ϕ is completely unknown, and therefore the position of the oscillator is not known. One therefore has to resort to determining the probability that the position of the oscillator lies between x and $x + dx$.

(a) This probability must be proportional to the time the oscillator spends between x and $x + dx$. Find the speed of the oscillator at position x as a function of x, ω and x_0. Using this expression, determine the probability $p(x)dx$ that the position of the oscillator is between x and $x + dx$.

(b) Let the energy of the oscillator lie between E and $E + \Delta E$, where $\Delta E << E$. Sketch the phase space and the region accessible to the particle, calculating the volume of the accessible region. Next, compute the ratio of the volume of the accessible phase space corresponding to the position of the particle lying between x and $x + dx$ and the total volume of the accessible phase space. What does this result signify?

Solution 1:

(a) *The energy of the oscillator is* $E = m\omega^2 x_0^2/2$. *If the position of the oscillator is* x *and its speed is* v, *then*

$$\begin{aligned} \frac{1}{2}mv^2 + \frac{1}{2}m\omega^2 x^2 &= \frac{1}{2}m\omega^2 x_0^2 \\ \Longrightarrow v &= \omega\sqrt{x_0^2 - x^2} \end{aligned}$$

Since $dx/dt = v$, *therefore the time it spends between* x *and* $x + dx$ *is*

$$\begin{aligned} dt &= \frac{dx}{v} \\ &= \frac{dx}{\omega\sqrt{x_0^2 - x^2}} \end{aligned}$$

The probability that the position is between x *and* $x + dx$ *is then of the form*

$$P(x)dx = \frac{N dx}{\omega\sqrt{x_0^2 - x^2}}$$

where N *is a normalisation constant, to be determined by the constraint* $\int_{-x_0}^{x_0} dx P(x) = 1$. *Evaluating the integral gives* $N = \omega/\pi$. *Then*

$$P(x)dx = \frac{dx}{\pi\sqrt{x_0^2 - x^2}}$$

(b) *Given the relation*

$$\frac{p^2}{2m} + \frac{1}{2}m\omega^2 x^2 = E$$

the phase space trajectory corresponding to energy E *forms an ellipse in the* $p - x$ *plane, with the region of the phase space corresponding to energy lying between* E *and* $E + \Delta E$ *being the region between two ellipses. To compute the volume of this region, we first compute the area enclosed by the* *elliptical region corresponding to the energy lying between zero and E. Given the above equation, this volume (area, in this case) is easily computed to be*

$$\Gamma = \frac{2\pi E}{\omega}$$

Then the volume of the region corresponding to energy lying between E and $E + \Delta E$ is

$$\Delta\Gamma = \frac{2\pi \Delta E}{\omega}$$

The volume of the region corresponding to position lying between x and $x + dx$ is

$$\delta\Gamma = dxdp$$

where dp is computed using the relation between p, x and E. For a given x, p has two values, one positive and one negative. The volume is then twice the volume computed assuming that p is positive, given by

$$p = \sqrt{2mE - m^2\omega^2x^2}$$

Then

$$dp = \frac{m\Delta E}{\sqrt{2mE - m^2\omega^2x^2}}$$

Using the fact that $E = m\omega^2x_0^2/2$, we get

$$\delta\Gamma = \frac{2\Delta E}{\omega}\frac{dx}{\sqrt{x_0^2 - x^2}}$$

Then

$$\frac{\delta\Gamma}{\Delta\Gamma} = \frac{dx}{\pi\sqrt{x_0^2 - x^2}}$$

which is the same as the probability of the oscillator's position lying between x and $x + dx$.

Problem 2: Consider an isolated system of four non-interacting spins labelled 1, 2, 3, and 4, each with magnetic moment m, interacting with an external magnetic field B. Each spin can be parallel ('up') or antiparallel ('down') to B, with the energy of a spin parallel to B equal to $\epsilon = -mB$ and the energy of a spin antiparallel to B equal to $\epsilon = +mB$. Let the total energy of the system be $E = -2mB$.

(a) How many microstates of the system correspond to this macrostate? Enumerate these microstates.

(b) What is the probability that the system is in a given microstate in equilibrium?

(c) What is the probability that a given spin points up? Use this probability to campute the mean magnetic moment of a given spin in equilibrium.

(d) What is the probability that if spin 1 is 'up', spin 2 is also 'up'?

Solution 2: *Since the energy of the system is $E = -2mB$, the total magnetic moment of the system is $M = +2m$, which corresponds to one spin 'down' and three spins 'up'.*

(a) *The total number of microstates is then*

$$\begin{aligned}\Omega &= \frac{4!}{3! \times 1!} \\ &= 4\end{aligned}$$

(b) *The probability of any given microstate is*

$$\begin{aligned} P_r &= \frac{1}{\Omega} \\ &= \frac{1}{4} \end{aligned}$$

(c) *Given that a particular spin is 'up', there are three microstates corresponding to this (corresponding to one of the remaining spins being 'down'). Therefore, the probability is*

$$P_u = \frac{3}{4}$$

and the probability of the given spin being 'down' is

$$P_d = \frac{1}{4}$$

The mean magnetic moment of a give spin is

$$\begin{aligned} \overline{m} &= m \times P_u + (-m) \times P_d \\ &= \frac{m}{2} \end{aligned}$$

(d) *Given that spin 1 is up, there are in all three microstates corresponding to this. Of these, two correspond to spin 2 also being up. Therefore, the propbability that spin 2 is also up is*

$$P_{1u|2u} = \frac{2}{3}$$

Problem 3: Consider a system of four non-interacting distinguishable particles, with each particle localised to a lattice site. The energy of each particle is is restricted to values $\epsilon = 0, \epsilon_0, 2\epsilon_0, 3\epsilon_0, ...$ The system is divided into two subsystems A and B, subsystem A consisting of particles 1 and 2, and B consisting of particles 3 and 4 respectively. A and B are initially thermally insulated from each other, with energies $E_A = 5\epsilon_0$ and $E_B = \epsilon_0$. What are the possible microstates of the composite system? Now, suppose the two subsystems are allowed to thermally interact with each other, so that they can exchange energy without the total energy of the system changing. After equilibrium is attained, enumerate the possible microstates of the composite system. In equilibrium, what is the probability that subsystem A has energy E_A, for $E_A = 0, \epsilon_0, 2\epsilon_0, .., 6\epsilon_0$? For what value of E_A is the probability maximum?

Solution 3: *Let us denote the microstates of the composite system as* $(-,-|-,-)$ *where the first two slots are for system A and the second two slots for system B. Given that system A has energy* $5\epsilon_0$ *and system B has energy* ϵ_0 *gives the following 12 microstates for the composite system:*
$(0,5|0,1), (0,5|1,0), (5,0|0,1), (5,0|1,0), (1,4|0,1), (1,4|1,0), (4,1|0,1), (4,1|1,0), (2,3|0,1), (2,3|1,0), (3,2|0,1)$ *and* $(3,2|1,0)$*, where all numbers are in units of* ϵ_0*. Once the system reaches equilibrium, the total number of microstates is given by the total number of ways of distributing energy* $6\epsilon_0$ *among* 4 *particles.*

$$\begin{aligned} \Omega &= \frac{(6+4-1)!}{6!(4-1)!} \\ &= \frac{9!}{6!3!} \\ &= 84 \end{aligned}$$

The probability that system A has energy E_A *is given by the product of the number of microstates of system A corresponding to its energy being* E_A *and the number of microstates of system B corresponding* *to its energy being* $E_B = E - E_A$*, divided by the total number of microstates (here,* $E = 6\epsilon_0$*). For example, let* $E_A = \epsilon$*. Then, the number of microstates accessible to* A *corresponding to this is 2. The energy available to system* B *is* 5ϵ*, which can be distributed among 2 particles in 6 different ways. Then, the total number of microstates corresponding to system* A *having this energy is* $\Omega(E_A = \epsilon_0) = 2 \times 6 = 12$*. The probability of this is then*

$$\begin{aligned} P(E_A = \epsilon_0) &= \frac{\Omega(E_A = \epsilon_0)}{\Omega} \\ &= \frac{12}{84} \\ &= \frac{1}{7} \end{aligned}$$

Similarly, probabilities of other possible values of energy can be computed, and it can be checked that the probability is maximum for $E_A = 3\epsilon_0$*, and is equal to* $4/21$*.*

1.2 Entropy and Thermodynamic Probability

Problem 1: Consider a system of N particles (which could be interacting with each other) with energy E and occupying a volume V. The entropy of the system is known to be extensive. Suppose the energy of the system is changed, such that the new energy is λE, where λ is a multiplicative factor. Can you say that the new entropy will be λS, where S is the original entropy? If not, what other changes will be needed such that this is true?

Solution 1: *Since entropy is extensive, therefore, entropy will be* λS *under* $N \to \lambda N, V \to \lambda V$ *and* $E \to \lambda E$ *simultaneously.*

Problem 2: Consider a system of $N >> 1$ weakly interacting particles, each of which can be in quantum states with energies $0, \epsilon, 2\epsilon, 3\epsilon, ...$ Given the system has a certain energy, the temperature of the system is given by

$$\begin{aligned} \frac{1}{T} &= \frac{\partial S}{\partial E} \\ &\simeq \frac{\Delta S}{\Delta E} \end{aligned}$$

where ΔS is the change in the entropy of the system due to the change in the energy of the system by ΔE.

(a) If the system is in its ground state, what is its entropy?

(b) If the total energy of the system is ϵ, what is its entropy?

(c) What is the change in entropy of the system if the total energy of the system is increased from ϵ to 2ϵ?

(d) Given the above definition of temperature, what is the temperature of the system if its total energy is ϵ?

Solution 2:

(a) *The ground state corresponds to a unique microstate, in which all the particles have energy 0. Its entropy, therefore, is zero.*

(b) *If the total energy is ϵ, there are N possible microstates corresponding to this, in which one particle has energy ϵ and others have energy 0. The entropy is $S = k_B \ln N$.*

(c) *If the total energy is 2ϵ, this corresponds to either two particles with energy ϵ (which corresponds to $N(N-1)/2$ possible microstates) or one particle with energy 2ϵ (which corresponds to N possible microstates). Therefore, the total number of microstates is $\Omega = N + N(N-1)/2 = N(N+1)/2$. Then, the entropy of the system is*

$$\begin{aligned} S' &= k_B \ln\left(N(N+1)/2\right) \\ &\simeq k_B \ln N + k_B \ln(N/2) \quad (\because N >> 1) \end{aligned}$$

Then, the change in entropy is $\Delta S = k_B \ln(N/2)$.

(d) *The temperature of the system is given by*

$$\begin{aligned} \frac{1}{T} &\simeq \frac{\Delta S}{\Delta E} \\ &= \frac{k_B}{\epsilon} \ln(N/2) \end{aligned}$$

Therefore,

$$T = \frac{\epsilon}{k_B} \frac{1}{\ln(N/2)}$$

Problem 3: A system of four weakly interacting distinct particles is such that each particle can be in one of four states with energies $\epsilon, 2\epsilon, 3\epsilon$ and 4ϵ respectively. If the system has total energy 15ϵ, what is the entropy of the system? For what possible values of total energy is the entropy of the system zero?

Solution 3: Since the total energy of the system is 15ϵ, this corresponds to three particles with energy 4ϵ and one particle with energy 3ϵ. There are four microstates corresponding to this. Therefore, the entropy of the system is $S = k_B \ln 4$. The entropy of the system is zero if either the total energy of the system is 4ϵ or 16ϵ, since these macrostates correspond to one microstate each.

Problem 4: Consider a lattice of N non-interacting distinguishable particles, with each particle localised to a lattice site. The energy of each particle is restricted to values $\epsilon = 0, \epsilon_0, 2\epsilon_0, 3\epsilon_0, ...$ The system is in equilibrium.

(a) If the energy of the system is E, what is the number of microstates of the system?

(b) Find an expression for the entropy of the system as a function of energy and simplify it using Sterling's approximation $\ln n \simeq n \ln n - n$ for $n >> 1$.

(c) Using the relation

$$\frac{1}{T} = \frac{\partial S}{\partial E}$$

determine a relation between the energy of the system and its temperature.

Hint: The problem of determining the number of microstates can be reduced to counting the number of ways of arranging a certain number of sticks and a certain number of dots along a line.

Solution 4:

(a) *A microstate of the system can be represented as the set* $(n_1, n_2, .., n_N)$ *which represents a state in which the first particle has energy* $n_1\epsilon_0$*, second has energy* $n_1\epsilon_0$*,... Let* $M = E/\epsilon$*. Then,*

$$n_1 + n_2 + ..n_N = M$$

The total number of microstates is the number of ways of choosing integers $n_1, n_2, .., n_N$ *such that their sum is* M*. This is the same as the number of ways of partitioning* M *into* N *parts. This can be visualised as the number of ways* M *dots and* $N - 1$ *sticks can be arranged in a line, the sticks creating partitions. Therefore, the number of microstates is*

$$\begin{aligned}\Omega(E) &= \frac{(M+N-1)!}{M!(N-1)!} \\ &= \frac{(E/\epsilon + N - 1)!}{(E/\epsilon)!(N-1)!} \\ &\simeq \frac{(E/\epsilon + N)!}{(E/\epsilon)!N!}\end{aligned}$$

assuming $E, N >> 1$.

(b) *The entropy of the system is*

$$\begin{aligned}S &= k_B \ln \Omega \\ &\simeq k_B \left[\left(\frac{E}{\epsilon} + N\right) \ln \left(\frac{E}{\epsilon} + N\right) - \frac{E}{\epsilon} \ln \frac{E}{\epsilon} - N \ln N\right]\end{aligned}$$

where Sterling's approximation has been used.

(c) *The temperature of the system is given by*

$$\begin{aligned}\frac{1}{T} &= \frac{\partial S}{\partial E} \\ &= \frac{k_B}{\epsilon} \ln \left(1 + \frac{N\epsilon}{E}\right)\end{aligned}$$

which is inverted to give

$$E = \frac{N\epsilon}{e^{\epsilon/k_B T} - 1}$$

1.3 Maxwell Boltzmann Distribution

Problem 1: Consider atomic hydrogen in thermal equilibrium at temperature T. Estimate the ratio of the number of atoms with energy $E = -3.4$ eV to the number of atoms with energy $E = -13.6$ eV for $T = 1000°K$.

Solution 1: It is useful to determine the temperature equivalent to energy equal to 1ev. This temperature is

$$\begin{aligned}T_{ev} &= \frac{1 \text{ ev}}{k_B} \\ &= 1.16 \times 10^4 \ {}^\circ K\end{aligned}$$

There are two microstates corresponding to the atom in its ground state (with energy -13.6 eV) corresponding to the two spin states of the electron. Similarly, there are eight microstates corresponding to the first excited states (with energy −3.4 eV). Then, the relative probability of the atom being in one of the first excited states is

$$\begin{aligned}\frac{P_{exc}}{P_{gr}} &= \frac{8\times e^{3.4ev/k_BT}}{2\times e^{13.6ev/k_BT}}\\ &= 4e^{-10.2ev/k_BT}\\ &= 4e^{-10.2\ T_{ev}/T}\\ &= 4e^{-118.32}\end{aligned}$$

which is vanishingly small.

Problem 2: A system of N weakly interacting particles, each of mass m, is in thermal equilibrium at temperature T. The system is contained in a cubical box of side L, whose top and bottom surfaces are parallel to the Earth's surface, where the acceleration due to gravity is g. A coordinate system is set up with the origin at the centre of the base of the box and the positive z axis along the vertical direction, such that the ranges of coordinates accessible to any particle are $-L/2 \le x \le L/2$, $-L/2 \le y \le L/2$, $0 \le z \le L$.

(a) What is the probability that a given particle has velocity in the range (v_x, v_y, v_z) and $(v_x + dv_x, v_y + dv_y, v_z + dv_z)$?

(b) What is the probability that a given particle has x coordinate between x and $x + dx$?

(c) What is the probability that a given particle has y coordinate between y and $y + dy$?

(d) What is the probability that a given particle has z coordinate between z and $z + dz$?

(e) From the above probability distributions, calculate the mean kinetic and potential energies of a particle.

Solution 2: *The probability of a microstate of a particle corresponding to its position lying between* (x, y, z) *and* $(x + dx, y + dy, z + dz)$ *and velocity between* (v_x, v_y, v_z) *and* $(v_x + dv_x, v_y + dv_y, v_z + dv_z)$ *is given by the Maxwell Boltzmann distribution*

$$P(x,y,z,v_x,v_y,v_z)dxdydzdv_xdv_ydv_z = Ne^{-\beta[m(v_x^2+v_y^2+v_z^2)/2+mgz]}$$

where N *is a normalisation constant such that* $\int Pdxdydzdv_xdv_ydv_z = 1$. *The integral over velocity components is Gaussian and gives* $(2\pi/m\beta)^{3/2}$. *The integral over position coordinates gives*

$$\begin{aligned}I &= \int_{-L/2}^{L/2} dxdy \int_0^L dze^{-\beta mgz}\\ &= \frac{L^2}{\beta mg}\left(1-e^{-\beta mgL}\right)\end{aligned}$$

Then, the normalisation constant is determined to be

$$N = \left(\frac{m\beta}{2\pi}\right)^{3/2}\frac{\beta mg}{L^2\left(1-e^{-\beta mgL}\right)}$$

(a)

$$\begin{aligned}P(v_x,v_y,v_z)dv_xdv_ydv_z &= dv_xdv_ydv_z\int dxdydzP(x,y,z,v_x,v_y,v_z)\\ &= \left(\frac{m\beta}{2\pi}\right)^{3/2} e^{-\beta m(v_x^2+v_y^2+v_z^2)/2}dv_xdv_ydv_z\end{aligned}$$

which is just the Maxwell velocity distribution.

(b)

$$\begin{aligned} P(x)dx &= dx\int dydzdv_xdv_ydv_zP(x,y,z,v_x,v_y,v_z) \\ &= \frac{dx}{L} \end{aligned}$$

(c)

$$\begin{aligned} P(y)dy &= dy\int dxdzdv_xdv_ydv_zP(x,y,z,v_x,v_y,v_z) \\ &= \frac{dy}{L} \end{aligned}$$

(d)

$$\begin{aligned} P(z)dz &= dz\int dxdydv_xdv_ydv_zP(x,y,z,v_x,v_y,v_z) \\ &= \frac{\beta mg}{(1-e^{-\beta mgL})}e^{-\beta mgz}dz \end{aligned}$$

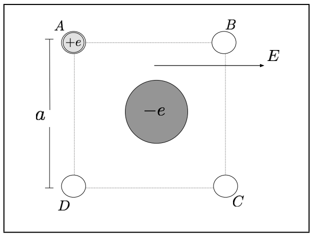
(e) *The mean kinetic energy is*

$$\begin{aligned} \overline{K} &= 3\times\frac{1}{2}m\overline{v_x^2} \\ &= 3\times\frac{1}{2}m\int dv_xP(v_x)v_x^2 \\ &= 3\times\frac{1}{2}m\left(\frac{m\beta}{2\pi}\right)^{1/2}\int dv_xv_x^2e^{-\beta mv_x^2/2} \\ &= \frac{3}{2\beta} \end{aligned}$$

The mean potential energy is

$$\begin{aligned} \overline{U} &= mg\overline{z} \\ &= mg\int_0^L dz\ zP(z) \\ &= mg\frac{\beta mg}{(1-e^{-\beta mgL})}\int_0^L dzz\ e^{-\beta mgz} \\ &= \frac{1}{\beta}\left[1-\frac{\beta mgL}{(e^{\beta mgL}-1)}\right] \end{aligned}$$

Problem 3: A two-dimensional solid at temperature T contains N negatively charged impurity ions per unit area, the negative ions replacing some ordinary atoms of the solid. The solid as a whole is electrically neutral, since each negative ion with charge $-e$ has in its vicinity one positive ion with charge $+e$. The positive ion, much smaller, is free to move between each of the four equidistance sites A, B, C and D surrounding the stationary negative ion, as shown. The spacing between the these sites is a and the energy of interaction of the positive ion with the stationary negative ion is $-\epsilon_0$ for each lattice site



(a) What are the relative probabilities of the positive ion being found at the four lattice sites?

(b) The solid is placed in a region of a uniform electric field of magnitude E, as illustrated above. Taking the origin at the location of the negative ion, determine the interaction energy of the system with the external electric field at the four lattice sites (*the interaction energy is* $E_{int} = -\vec{p} \cdot \vec{E}$ *where* $\vec{p}$ *is the dipole moment of the system*).

(c) What now are the relative probabilities of the positive ion being found at the four lattice sites?

(d) The mean polarisation of the solid is the mean dipole moment per unit area along the direction of the electric field. Calculate the polarisation of the solid as a function of temperature and the external electric field E.

(e) Calculate the expression for the polarisation at 'high' temperatures. What temperatures are 'high'?

Solution 3: *The system has four microstates, corresponding to the four possible locations of the positive ion.*

(a) *In absence of an external electric field, each microstate has the same energy. Therefore, they are all equiprobable.*

(b) *The magnitude of the dipole moment of the system corresponding to each position of the positive ion is* $p_0 = ea/\sqrt{2}$*. Given that the interaction energy of a dipole is* $E_{int} = -\vec{p} \cdot \vec{E}$*, the energies of the four microstates are respectively* $\epsilon_A = \epsilon_D = +eaE/2$ *and* $\epsilon_B = \epsilon_C = -eaE/2$*.*

(c) *The probability of the ion being found at sites* A *and* D *are equal. Similarly, the probability of the ion being found at sites* B *and* C *are equal. The reltive probabilities of the ion being found at sites* A *and* B *is*

$$\begin{aligned}\frac{P_A}{P_B} &= \frac{e^{-\beta\epsilon_A}}{e^{-\beta\epsilon_B}} \\ &= e^{-\beta eaE}\end{aligned}$$

(d) *If the polarisation of the dipole at a lattice site is* $\vec{p}$*, the mean polarisation is the average value of* $p_{\parallel} = \vec{p} \cdot \hat{E}$*, where* $\hat{E}$ *is a unit vector along* $\vec{E}$*. The value of this quantity at the four lattice sites is* $p_{\parallel A} = p_{\parallel D} = -ea/2$ *and* $p_{\parallel B} = p_{\parallel C} = +ea/2$*. Given that* $P_A + P_B + P_C + P_D = 1$ *and given the ratio* P_A/P_B*, the probabilities are computed to be*

$$\begin{aligned}P_A &= \frac{1}{2}\left(\frac{1}{1+e^{\beta eaE}}\right) \\ P_B &= \frac{1}{2}\left(\frac{e^{\beta eaE}}{1+e^{\beta eaE}}\right)\end{aligned}$$

Then,

$$\begin{aligned}\overline{p_{\parallel}} &= 2P_A p_{\parallel A} + 2P_B p_{\parallel B} \\ &= \frac{ea}{2}\left(\frac{e^{\beta eaE}-1}{e^{\beta eaE}+1}\right) \\ &= \frac{ea}{2}\tanh\left(\frac{\beta eaE}{2}\right)\end{aligned}$$

Since there are N impurities per unit area, therefore, the mean polarisation is

$$\begin{aligned}\overline{P} &= N\overline{p_{\parallel}} \\ &= \frac{Nea}{2}\tanh\left(\frac{\beta eaE}{2}\right)\end{aligned}$$

'High' temperatures correspond to the condition $\beta eaE/2 << 1$. Under such conditions,

$$\begin{aligned}\overline{P} &\simeq \frac{Nea}{2}\left(\frac{\beta eaE}{2}\right) \\ &= N\frac{(ea)^2E}{4k_BT}\end{aligned}$$

Problem 4: A sensitive spring balance consists of a quartz spring with spring constant k. This balance is used to measure the mass of very tiny, light objects by suspending them from the balance and observing the extension in the spring. Consider a tiny object of mass m suspended from the spring. The object is in an environment which is at temperature T, and gets 'kicked' around by it, reaching equilibrium with the environment.

1. What is the potential energy of the system if the spring is extended by x?
2. What is the probability that the spring is extended by x relative to its equilibrium length?
3. Calculate the mean extension $\overline{x}$ and the mean squared extension $\overline{(x-\overline{x})^2}$.
4. Comparing the square root of the mean squared extension with the mean extension, extimate the minimum mass that can be reliably measured.

Solution 4:

(a) *If the position of the mass relative to the relaxed position of the spring is x, then its potential energy is*

$$\begin{aligned}U(x) &= \frac{1}{2}kx^2 + mgx \\ &= \frac{1}{2}k(x+x_0)^2 - \frac{m^2g^2}{2k}\end{aligned}$$

where $x_0 = mg/k$.

(b) *The probability of the position of the mass lying between x and $x+dx$ is*

$$P(x)dx = Ne^{-\beta U(x)}dx$$

where N is determined by the normalisation condition $\int_{-\infty}^{\infty} dxP(x) = 1$. The integral is a Gaussian, resulting in

$$P(x)dx = \sqrt{\frac{\beta k}{2\pi}}e^{-\beta k(x+x_0)^2/2}dx$$

(c) *The mean extension is clearly $\overline{x} = -x_0$. The mean square extension is*

$$\begin{aligned}\overline{(x-\overline{x})^2} &= \int_{-\infty}^{\infty} dx(x+x_0)^2P(x) \\ &= \frac{k_BT}{k}\end{aligned}$$

(d) *The fluctuation in position is* $\Delta x = \sqrt{\overline{(x-\overline{x})^2}}$. *For the measurement to be reliable,* $\Delta x << x_0$. *This results in the condition*

$$m >> \frac{1}{g}\sqrt{k_B T k}$$

1.4 Partition Function, Heat Capacity, Entropy

Problem 1: Consider a single particle system with five states. There is one state with energy 0, two states with energy ϵ and two states with energy 2ϵ. The system is in equilibrium with a heat bath at temperature T.

(a) Calculate the partition function for the system.

(b) Calculate the mean energy and heat capacity of the system as functions of temperature.

(c) What is the relative probability of the system having energy 2ϵ and ϵ?

Problem 2: The partition function of a system is given by

$$lnZ = aT^4V$$

where T is the absolute temperature, V is the volume of the system and a is a constant. Evaluate the mean energy, pressure and entropy of the system.

Problem 3: Consider a simplified model of graphite, in which each carbon atom acts as a harmonic oscillator, oscillating with frequency ω within the layer and frequency ω' perpendicular to it. The oscillations in the three directions are independent, such that the expression for energy of a carbon atom is

$$E = \frac{1}{2m}(p_x^2 + p_y^2 + p_z^2) + \frac{m}{2}(\omega^2 x^2 + \omega^2 y^2 + \omega'^2 z^2)$$

where coordinates x, y are in the plane of the layer and z is perpendicular to it. The sample is at temperature T, such that $\hbar\omega >> T$ and $\hbar\omega' << T$ (the restoring forces in the plane of the layer are much stronger than those perpendicular to it).

(a) Given the temperature conditions, one kind of the oscillations (in the plane or perpendicular to it) can be treated classically, and the other quantum mechanically with only the ground and first excited states appreciably populated. Identify the corresponding oscillations.

(b) Taking into account the above considerations, calculate the partition function and show that it factorises into three factors, two of which are identical.

(c) Find an expression for the molar specific heat of the system as a function of temperature, using approximations appropriate to the temperature conditions stated above.

Solution 3:

(a) *Given the temperature conditions, the oscillations perpendicular to the plane can be treated classically, and those in the plane need to be treated quantum mechanically.*

(b) *Since the expression for energy is additive in the contributions along the three independent directions, the partition function for each atom will factorise as*

$$Z = Z_x Z_y Z_z$$

where further, $Z_x = Z_y$. Given that the motion perpendicular to the plane can be treated classically, it follows that

$$\begin{aligned} Z_z &= \int dz dp_z e^{-\beta(p_z^2/2m+m\omega'^2 z' 2)} \\ &= \frac{2\pi}{\omega'\beta} \end{aligned}$$

For the motion in the plane, given that $\hbar\omega >> T$, only the ground and the first excited state contributions are relevant. Then

$$\begin{aligned} Z_x &= \sum_{n=0}^{1} e^{-\beta(n+1/2)\hbar\omega} \\ &= e^{-\beta\hbar\omega/2} + e^{-3\beta\hbar\omega/2} \\ &= e^{-\beta\hbar\omega/2}\left(1+e^{-\beta\hbar\omega}\right) \end{aligned}$$

Finally, the partition funciton for a single atom is

$$\begin{aligned} Z &= Z_x^2 Z_z \\ &= e^{-\beta\hbar\omega}\left(1+e^{-\beta\hbar\omega}\right)^2\left(\frac{2\pi}{\omega'\beta}\right) \end{aligned}$$

(c) *The logarithm of the partition function is*

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

The mean energy per atom is

$$\begin{aligned} \bar{\epsilon} &= -\frac{\partial \ln Z}{\partial \beta} \\ &= \hbar\omega + k_B T + \frac{2\hbar\omega}{1+e^{\beta\hbar\omega}} \end{aligned}$$

The heat capacity per atom is

$$\begin{aligned} c &= \frac{\partial \epsilon}{\partial T} \\ &= k_B\left[1 + 2\left(\frac{\hbar\omega}{k_B T}\right)^2 \frac{1}{\left(1+e^{\hbar\omega/k_B T}\right)^2}\right] \end{aligned}$$

Therefore, the molar specific heat of the system will be

$$C = R\left[1 + 2\left(\frac{\hbar\omega}{k_B T}\right)^2 \frac{1}{\left(1+e^{\hbar\omega/k_B T}\right)^2}\right]$$

Problem 4: N diatomic molecules are stuck on a surface. Each molecule can either lie flat on the surface (in which case it can orient itself either along the x or the y direction) or it can stand up perpendicular to the surface (along the z direction). Assume that the flat configurations have zero energy and the configuration perpendicular to the surface has energy $\epsilon > 0$. The system is in thermal equilibrium at temperature $T > 0$.

(a) Calculate the partition function of the system.

(b) Calculate the mean energy of the system. What is the largest possible value for this energy (attained by changing the temperature)?

(c) Calculate the heat capacity of the system as a function of temperature.

(d) What is the probability of a given molecule 'standing up'?

Solution 4: *For each molecule, there are three microstates corresponding to it oriented along the* x, y *or* z *directions. The energies of these microstates are* $\epsilon_x = \epsilon_y = 0$, $\epsilon_z = \epsilon$.

(a) *The partition function for a single molecule is*

$$\begin{aligned} Z_1 &= 1 + 1 + e^{-\beta\epsilon} \\ &= 2 + e^{-\beta\epsilon} \end{aligned}$$

Then, since the molecules are independent, the partition fucntion of the system is

$$\begin{aligned} Z &= Z_1^N \\ &= \left(2 + e^{-\beta\epsilon}\right)^N \end{aligned}$$

(b) *The mean energy of the system is*

$$\begin{aligned} \overline{E} &= -\frac{\partial \ln Z}{\partial \beta} \\ &= \frac{N\epsilon}{1 + 2e^{\beta\epsilon}} \end{aligned}$$

As $T \to \infty, \beta \to 0$. *In this limit,* $\overline{E} \to N\epsilon/3$.

(c) *The heat capacity of the system is*

$$\begin{aligned} C &= \frac{\partial \overline{E}}{\partial T} \\ &= 2Nk_B \left(\frac{\epsilon}{k_B T}\right)^2 \frac{e^{\beta\epsilon}}{1 + 2e^{\beta\epsilon}} \end{aligned}$$

(d) *The probability of a given molecule standing 'up' is*

$$\begin{aligned} P_z &= \frac{1}{Z_1} e^{-\beta\epsilon} \\ &= \frac{1}{1 + 2e^{\beta\epsilon}} \end{aligned}$$

1.5 Negative Temperatures

Problem 1: Consider an isolated system of $N >> 1$ weakly interacting, distinct particles in equilibrium. Each particle can be in one of three states, with energies $0, \epsilon$ and 2ϵ respectively. Given the system has a certain energy, the temperature of the system is given by

$$\begin{aligned} \frac{1}{T} &= \frac{\partial S}{\partial E} \\ &\simeq \frac{\Delta S}{\Delta E} \end{aligned}$$

where ΔS is the change in the entropy of the system due to the change in the energy of the system by ΔE.

(a) Let the entire system be in its ground state. What is its entropy? If the anergy $\Delta E = \epsilon$ is added to the system, what is its entropy? Given the definition of temperature above, what can you say about the temperature of the system if it is in the ground state?

(b) Let the total energy of the system be $2N\epsilon - \epsilon$. What is the entropy of the system? What is the entropy of the system if energy $\Delta E = \epsilon$ is added to it? If the system has energy $2N\epsilon - \epsilon$, what can you say about the temperature of the system?

Solution 1:

(a) *If the system is in its ground state, there is only one microstate corresponding to this (all particles with energy* 0*). Therefore, the entropy of the system is zero. If energy* $\Delta E = \epsilon$ *is added to it, the energy of the system is* ϵ*. This corresponds to* N *possible microstates, in which one particle has energy* ϵ *and all others have energy* 0*. Then, the entropy of the system is* $S = k_B \ln N$*. The temperature of the system in the ground state is positive, since an increase in energy increases entropy.*

(b) *If the total energy of the system is* $2N\epsilon - \epsilon$*, this corresponds to* N *microstates in which one particle has energy* ϵ *and all others have energy* 2ϵ*. The entropy of the system is then* $S = k_B \ln N$*. If energy* ϵ *is added to the system, the number of microstates reduces to one, corresponding to all the particles having energy* 2ϵ*. The entropy therefore reduces to zero. Since addition of energy decreases entropy, the temperature of the system is negative.*

Problem 2: Consider an isolated system of $N >> 1$ weakly interacting, distinct particles in equilibrium. Each particle can be in one of M states with energies $\epsilon_0, 2\epsilon_0, ..., M\epsilon_0$. Can this system exhibit negative temperatures? If so, give a value of energy corresponding to which the temperature of the system is (a) positive (b) negative. (c) If $M \longrightarrow \infty$, will the system exhibit negative temperatures? Give a physical argument.

Solution 2: *The system does exhibit negative temperatures, since the energy of the system is bounded from above, the maximum possible energy being* $NM\epsilon_0$*. (a) The system in the ground state has a positive temperature, since adding energy* ϵ_0 *to the system increases its entropy by* $\Delta S = k_B \ln N$*. (b) The system, when its energy is* $MN\epsilon_0 - \epsilon_0$*, has a negative temperature, since increasing its energy by* ϵ_0 *decreses its entropy by* $\Delta S = -k_B \ln N$*. (c) As* $M \to \infty$*, increasing the energy of the system will always increase its entropy. Therefore, the system will always have a positive temperature.*

Problem 3: Consider two systems A and B, system A consisting of $N_A >> 1$ weakly interacting particles, each of which can be in one of an infinite number of possible quantum states with energies $0, \epsilon, 2\epsilon, 3\epsilon, ...$ System B on the other hand consisting of $N_B >> 1$ weakly interacting particles, each of which can be in one of two quantum states with energies $0, \epsilon$. Initially, these systems are insulated from each other, with system A having total energy $N_A\epsilon$ and B having energy $3N_B\epsilon/4$.

(a) What can you say about the sign of the temperatures of these two systems?

(b) The systems are now made to interact with each other, till they reach equilibrium. What is the sign of the temperature of each system after equilibrium is attained?

Solution 3:

(a) *Since the energy of system A is not bounded from above, it will always have a positive temperature. System B, on the other hand, can exhibit both positive and negative temperatures. It will have a negative temperature for energies greater than $N_B\epsilon/2$, since for energies greater than this, increasing the energy of the system will decrease its entropy. Given that its energy is $3N_B\epsilon/4$, it has a negative temperature.*

(b) *After the systems interact and attain equilibrium, since system A always has a positive temperature, system B will be driven to a positive temperature as well, as a result of losing a part of its energy to system A to maximise the overall entropy.*

1.6 Equipartition Principle

Problem 1: Consider a classical system of $N >> 1$ independent oscillators, each of which has energy given by

$$\epsilon = \frac{p^2}{2m} + \frac{1}{2}kx^2$$

where x and p are the position and momentum of the particle. If the system is in equilibrium at temperature T, what is the molar specific heat of the system? If the expression for energy has a small correction which is not quadratic in x, what will be the qualitative change in the behaviour of the specific heat of the system?

Solution 1: *From the Equipartition Principle, the molar specific heat of the system will be $c_v = R$. If there is a non-quadratic correction, the Equipartition Principle is not applicable, and the molar specific heat will in general depend on the temperature.*

Problem 2: Consider a classical system of $N >> 1$ weakly interacting particles, each of which has energy given by

$$\epsilon = \frac{p^2}{2m} + \frac{1}{2}kx^2 + \lambda x^4$$

where x and p are the position and momentum of the particle. The system is in equilibrium at temperature T.

(a) If $\lambda = 0$, what is the moler specific heat of the system?

(b) If λ is not zero, but the quartic term is very 'small' compared to the quadratic term, what will be the variation in the specific heat of the system with temperature? *Hint: Use $e^u \simeq 1 + u$ for 'small' u.*

Solution 2:

(a) *If $\lambda = 0$, the energy is quadratic in position and momentum. Therefore, the Principle of Equipartition is valid, and the molar specific heat of the system will be $c_v = R$.*

(b) *If $\lambda \neq 0$, the partition function of the system will be*

$$\begin{aligned} Z &= \int dx dp\ e^{-\beta(p^2/2m + kx^2/2 + \lambda x^4)} \\ &\simeq \int dx dp\ e^{-\beta(p^2/2m + kx^2/2)} \left(1 - \beta\lambda x^4\right) \quad \text{since the correction to energy is `small'} \\ &= \frac{2\pi}{\beta}\sqrt{\frac{m}{k}} - \beta\lambda\sqrt{\frac{2m\pi}{\beta}} \times \int_{-\infty}^{\infty} dx\ x^4\ e^{-\beta k x^2/2} \\ &= \frac{2\pi}{\beta}\sqrt{\frac{m}{k}} - \beta\lambda\sqrt{\frac{2m\pi}{\beta}} \times \frac{3\sqrt{\pi}}{4}\left(\frac{2}{\beta k}\right)^{5/2} \\ &= \frac{2\pi}{\beta}\sqrt{\frac{m}{k}}\left(1 - \frac{3\lambda}{\beta k^2}\right) \end{aligned}$$

Therefore

$$\begin{aligned} \ln Z &= \ln Z_0 + \ln\left(1 - \frac{3\lambda}{\beta k^2}\right) \\ &\simeq \ln Z_0 - \frac{3\lambda}{\beta k^2} \quad (\because \text{correction is `small'}) \end{aligned}$$

where Z_0 is the partition function without the correction. The mean energy per particle is

$$\begin{aligned} \overline{\epsilon} &= -\frac{\partial \ln Z}{\partial \beta} \\ &= \overline{\epsilon_0} - \frac{3\lambda(k_B T)^2}{k^2} \end{aligned}$$

where $\overline{\epsilon_0}$ is the mean energy paer particle if $\lambda = 0$. The heat capacity per particle is

$$\begin{aligned} c &= \frac{\partial \overline{\epsilon}}{\partial T} \\ &= c_0 - \frac{6k_B\lambda(k_B T)}{k^2} \end{aligned}$$

Therefore, the molar specific heat of the system is

$$\begin{aligned} c_v &= N_A \times c \\ &= R - \frac{6R\lambda(k_B T)}{k^2} \\ &= R\left(1 - \frac{6\lambda(k_B T)}{k^2}\right) \end{aligned}$$

Problem 3: Consider a weakly interacting system of particles, such that the expression for energy of any one particle consists of n terms, quadratic in position and momentum components. If classical physics is an adequate description of this system, what is the molar specific heat of the system? If the temperature of the system is progressively lowered, will the experimentally measured molar specific heat be in agreement with this result? Explain.

Solution 3: *If Classical Physics is an adequate description, then the Principle of Equipartition can be applied, which gives the moolar specific heat to be $c_v = nR/2$. As the temperature is lowered, eventually, quantum effects become significant, and the molar specific heat will be found to be temperature dependent, in disagreement with the classical result.*

Thank you