1 The Failure of Classical Physics

At the beginning of the twentieth century, classical physics – Newtonian mechanics and electromagnetic theory (Maxwell's equations, wave phenomena, and optics) – could not explain a number of experimental facts, including the observed black-body radiation spectrum, the photoelectric effect, the stability of atoms and the associated spectral lines, the heat capacities of solids, and several others. The following problems are intended to illustrate the failure of classical physics to explain these phenomena and how this failure pointed to the need for a radically new treatment.

1.1 Problems

Problem 1 Black-Body Radiation Spectrum

Consider an enclosure of volume V whose walls are kept at temperature T, and define as $u(\nu, T)\, d\nu$ the energy density (energy per unit volume) of electromagnetic radiation in the frequency interval ν to $\nu + d\nu$. In the mid nineteenth century (at the height of classical physics!), Gustav Kirchoff was able to show, on the basis of purely thermodynamic arguments, that the distribution $u(\nu, T)$ has a universal character. He also calculated the energy per unit time of radiation of given frequency that strikes a small area A of the enclosure walls. He introduced polar coordinates r, θ, and ϕ, where r is the distance from a point P in the enclosure to the area A, the polar angle θ is measured from the normal to A and the azimuthal angle ϕ is measured around the normal to A. The area subtends a solid angle at P given by $A \cos\theta/r^2$ and the fraction of radiation energy from P that is directed to A is given by $A \cos\theta/(4\pi r^2)$. The total energy in the frequency interval ν to $\nu + d\nu$ that strikes the area A at time t is then obtained as

$$\int_0^{2\pi} d\phi \int_0^{\pi/2} d\theta\, \sin\theta \int_0^{ct} dr\, r^2\, \frac{A\cos\theta}{4\pi r^2}\, u(\nu, T)\, d\nu = \frac{ctA}{4}\, u(\nu, T)\, d\nu\ ,$$

where the integration is restricted to a hemisphere of radius ct, c being the speed of light, with θ varying in the range 0 to $\pi/2$. Given the finite velocity c of propagation, only radiation within this hemisphere will reach the area A in the time t. Denoting by $f(\nu, T)$ the fraction of this energy that is absorbed by the enclosure walls, we have that the total absorbed energy per unit time and area is

$$E(\nu, T) = \frac{c}{4}\, f(\nu, T)\, u(\nu, T)\, d\nu\ .$$

In a situation of equilibrium, $E(\nu, T)$ must equal the energy per unit time and area emitted by the enclosure walls in the same frequency interval. The fraction $f(\nu, T)$ of absorbed radiation can be at the most equal to unity. Indeed, a material for which $f(\nu, T) = 1$ is called black, and hence the name "black-body radiation" used to describe the present phenomenon.

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Electromagnetic radiation in an enclosure can be described in terms of an infinite set of uncoupled harmonic oscillators. The equipartition theorem of classical statistical mechanics then leads to a prediction for $u(\nu, T)$ that is in contradiction with the experimental data and produces nonsensical results in the limit of high frequency ν, leading to the so-called ultraviolet catastrophe. The goal of the present problem is to see how this comes about.

1. Write down Maxwell's equations for the electric and magnetic fields, $\mathbf{E}(\mathbf{r}, t)$ and $\mathbf{B}(\mathbf{r}, t)$, in the absence of charge and current distributions (use CGS units).
2. Consider the enclosure to be a cubical box of side $V^{1/3}$, and impose periodic boundary conditions on the fields, namely

$$\mathbf{E}(x + V^{1/3}, y, z, t) = \mathbf{E}(x, y, z, t) , \qquad \mathbf{B}(x + V^{1/3}, y, z, t) = \mathbf{B}(x, y, z, t) ,$$

   and similarly for y and z. Given that the $\mathbf{E}$ and $\mathbf{B}$ components are periodic functions, they can be expanded in Fourier series of the form

$$E_i(\mathbf{r}, t) = \sum_{\mathbf{k}} \widetilde{E}_i(\mathbf{k}, t)\, e^{i\mathbf{k}\cdot\mathbf{r}} , \qquad B_i(\mathbf{r}, t) = \sum_{\mathbf{k}} \widetilde{B}_i(\mathbf{k}, t)\, e^{i\mathbf{k}\cdot\mathbf{r}} ,$$

   where the quantities carrying tildes are coefficients and the wave number $\mathbf{k} = (k_x, k_y, k_z)$ is given by

$$\mathbf{k} = \frac{2\pi}{V^{1/3}}\,\mathbf{n} , \qquad \mathbf{n} = (n_x, n_y, n_z) , \qquad n_i = 0, \pm 1, \pm 2, \ldots$$

   Insert these expansions into Maxwell's equations and show that $\widetilde{\mathbf{E}}(\mathbf{k}, t)$ satisfies

$$\frac{\partial^2 \widetilde{\mathbf{E}}(\mathbf{k}, t)}{\partial t^2} = -\omega_k^2\, \widetilde{\mathbf{E}}(\mathbf{k}, t) , \qquad \omega_k = c|\mathbf{k}| = c\,\frac{2\pi}{V^{1/3}}\,|\mathbf{n}| .$$

   How many independent directions of $\widetilde{\mathbf{E}}$ are there? Further, show how to obtain $\widetilde{\mathbf{B}}(\mathbf{k}, t)$.
3. In the limit of large $V^{1/3}$, the wave numbers $\mathbf{k}$ are densely distributed. Show that in this limit the number of independent harmonic oscillators (normal modes) in $d\mathbf{k}$ is as follows:

$$\text{number of modes in } d\mathbf{k} = \rho(\mathbf{k})\, d\mathbf{k} = 2\,\frac{V}{(2\pi)^3}\, d\mathbf{k} .$$

   Recalling that in classical statistical mechanics the average energy of a harmonic oscillator kept at temperature T is simply $k_B T$, where k_B is Boltzmann's constant, and that the frequency ν is related to the wave number $|\mathbf{k}|$ via $c|\mathbf{k}|/(2\pi)$, show that the energy density of radiation with frequencies between ν and $\nu + d\nu$ is given by the Rayleigh–Jeans law

$$u(\nu, T)\, d\nu = 8\pi\,\frac{k_B T}{c^3}\,\nu^2\, d\nu .$$

   For a fixed temperature the above prediction is in agreement with the data only for small values of the frequency; it fails spectacularly at larger values. Furthermore, the total energy density of the radiation, obtained by integrating over ν, is found to be infinite – the aforementioned ultraviolet catastrophe; see Fig. 1.1.
4. Following Einstein, suppose that the radiation energy of frequency ν is quantized in integer multiples of $h\nu$, where h is Planck's constant. Calculate the average energy of radiation of frequency ν, given that the probability that there are n quanta is

$$p_n = \frac{e^{-nh\nu/k_B T}}{\sum_{n=0}^{\infty} e^{-nh\nu/k_B T}} .$$

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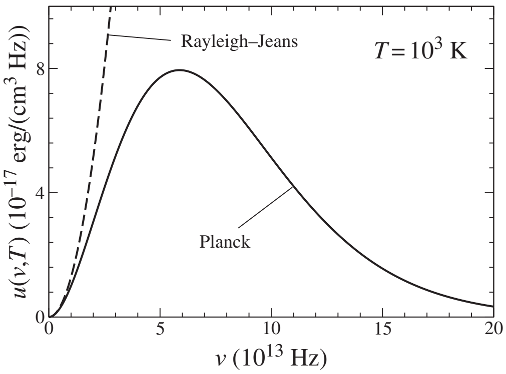

Fig. 1.1 The black-body radiation energy density per unit frequency: classical (Rayleigh–Jeans) versus quantum (Planck) description. The experimental data are in agreement with the quantum description.

Obtain the energy density in this case – the correct black-body radiation formula first derived by Planck. Show that the total energy density, that is, the energy density integrated over frequency ν, is proportional to T^4.

Solution

Part 1

In the absence of charge and current distributions, Maxwell's equations read (in the CGS system of units)

$$\nabla \cdot \mathbf{E}(\mathbf{r}, t) = 0\,, \qquad \nabla \times \mathbf{E}(\mathbf{r}, t) = -\frac{\partial \mathbf{B}(\mathbf{r}, t)}{c\,\partial t}\,,$$
$$\nabla \cdot \mathbf{B}(\mathbf{r}, t) = 0\,, \qquad \nabla \times \mathbf{B}(\mathbf{r}, t) = \frac{\partial \mathbf{E}(\mathbf{r}, t)}{c\,\partial t}\,,$$

where c is the speed of light.

Part 2

By inserting Fourier expansions into the set of Maxwell's equations, we obtain

$$\sum_{\mathbf{k}} i\,\mathbf{k} \cdot \widetilde{\mathbf{E}}(\mathbf{k}, t)\, e^{i\mathbf{k}\cdot\mathbf{r}} = 0\,, \qquad \sum_{\mathbf{k}} i\,\mathbf{k} \times \widetilde{\mathbf{E}}(\mathbf{k}, t)\, e^{i\mathbf{k}\cdot\mathbf{r}} = -\sum_{\mathbf{k}} \frac{\partial \widetilde{\mathbf{B}}(\mathbf{k}, t)}{c\,\partial t}\, e^{i\mathbf{k}\cdot\mathbf{r}}\,,$$
$$\sum_{\mathbf{k}} i\,\mathbf{k} \cdot \widetilde{\mathbf{B}}(\mathbf{k}, t)\, e^{i\mathbf{k}\cdot\mathbf{r}} = 0\,, \qquad \sum_{\mathbf{k}} i\,\mathbf{k} \times \widetilde{\mathbf{B}}(\mathbf{k}, t)\, e^{i\mathbf{k}\cdot\mathbf{r}} = \sum_{\mathbf{k}} \frac{\partial \widetilde{\mathbf{E}}(\mathbf{k}, t)}{c\,\partial t}\, e^{i\mathbf{k}\cdot\mathbf{r}}\,,$$

from which we deduce that the vectors $\widetilde{\mathbf{E}}$ and $\widetilde{\mathbf{B}}$ are perpendicular to the wave number $\mathbf{k}$,

$$\mathbf{k} \cdot \widetilde{\mathbf{E}}(\mathbf{k}, t) = 0\,, \qquad \mathbf{k} \cdot \widetilde{\mathbf{B}}(\mathbf{k}, t) = 0\,,$$

and satisfy the differential equations

$$\frac{\partial \widetilde{\mathbf{B}}(\mathbf{k}, t)}{c\,\partial t} = -i\,\mathbf{k} \times \widetilde{\mathbf{E}}(\mathbf{k}, t)\,, \qquad \frac{\partial \widetilde{\mathbf{E}}(\mathbf{k}, t)}{c\,\partial t} = i\,\mathbf{k} \times \widetilde{\mathbf{B}}(\mathbf{k}, t)\,.$$

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By taking the partial derivative $\partial/(c\,\partial t)$ of both sides of the second equation above, we find

$$\frac{\partial^2 \widetilde{\mathbf{E}}(\mathbf{k},t)}{c^2\,\partial t^2} = i\,\mathbf{k}\times\frac{\partial\widetilde{\mathbf{B}}(\mathbf{k},t)}{c\,\partial t} = i\,\mathbf{k}\times\left[-i\,\mathbf{k}\times\widetilde{\mathbf{E}}(\mathbf{k},t)\right] = \mathbf{k}\,\underbrace{\left[\mathbf{k}\cdot\widetilde{\mathbf{E}}(\mathbf{k},t)\right]}_{\text{vanishes}} - k^2\,\widetilde{\mathbf{E}}(\mathbf{k},t)\,,$$

where we have used the cross product property $\mathbf{A}\times(\mathbf{B}\times\mathbf{C}) = \mathbf{B}\,(\mathbf{A}\cdot\mathbf{C}) - \mathbf{C}\,(\mathbf{A}\cdot\mathbf{B})$. The equation above reduces to

$$\frac{\partial^2\widetilde{\mathbf{E}}(\mathbf{k},t)}{\partial t^2} = -\omega_k^2\,\widetilde{\mathbf{E}}(\mathbf{k},t)\,,\qquad \omega_k = c|\mathbf{k}| = c\,\frac{2\pi}{V^{1/3}}\,|\mathbf{n}|\,,$$

which shows that Maxwell's equations in the absence of sources are equivalent to an infinite set of uncoupled harmonic oscillators. The initial condition $\widetilde{\mathbf{E}}(\mathbf{k},t_0)$ and that on $\partial\widetilde{\mathbf{E}}(\mathbf{k},t)/\partial t$ at time t_0, which follows from $ic\,\mathbf{k}\times\widetilde{\mathbf{B}}(\mathbf{k},t_0)$, determine $\widetilde{\mathbf{E}}(\mathbf{k},t)$. For each wave number $\mathbf{k}$ and angular frequency ω_k there are two harmonic oscillators, corresponding to the two possible independent directions of the vector $\widetilde{\mathbf{E}}(\mathbf{k},t)$ in the plane perpendicular to $\mathbf{k}$, that is, the two independent polarizations of the electric field. Once the electric field $\widetilde{\mathbf{E}}(\mathbf{k},t)$ has been determined, the magnetic field $\widetilde{\mathbf{B}}(\mathbf{k},t)$ follows from direct integration of the equation obtained above,

$$\frac{\partial\widetilde{\mathbf{B}}(\mathbf{k},t)}{c\,\partial t} = -i\,\mathbf{k}\times\widetilde{\mathbf{E}}(\mathbf{k},t)\,.$$

Part 3

In the limit of large $V^{1/3}$, we can describe the distribution of modes with a function $\rho(\mathbf{k})$. Since there is a single wave number in each cell centered at $\mathbf{k}$ and with volume $(2\pi)^3/V$, given that the allowed $\mathbf{k}$ values are close to each other, the function $\rho(\mathbf{k})$ must satisfy the condition

$$\rho(\mathbf{k})\,\frac{(2\pi)^3}{V} = 2 \implies \rho(\mathbf{k}) = 2\,\frac{V}{(2\pi)^3}\,,$$

where the factor 2 accounts for the two independent polarizations associated with each given $\mathbf{k}$. We then obtain

$$\text{number of modes in } d\mathbf{k} = \rho(\mathbf{k})\,d\mathbf{k} = 2\,\frac{V}{(2\pi)^3}\,d\mathbf{k}\,,$$

and the energy density of radiation between ν and $\nu + d\nu$ is given by

$$u(\nu,T)\,d\nu = \frac{1}{V}\,k_B T\times(\text{number of modes in } d\nu)\,.$$

Recalling the relation between $|\mathbf{k}|$ and ν, it follows that

$$\text{number of modes in } d\nu = 2\,\frac{V}{(2\pi)^3}\,4\pi k^2\,dk = 8\pi\,\frac{V}{c^3}\,\nu^2\,d\nu\,,$$

yielding the Rayleigh–Jeans law for the energy density of radiation:

$$u(\nu,T)\,d\nu = 8\pi\,\frac{k_B T}{c^3}\,\nu^2\,d\nu\,.$$

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Part 4

Setting $\gamma = h\nu/(k_B T)$ for the time being, the average energy is now given by

$$\langle\text{energy}\rangle = h\nu \, \frac{\sum_{n=0}^{\infty} n e^{-n\gamma}}{\sum_{n=0}^{\infty} e^{-n\gamma}} = -h\nu \, \frac{d}{d\gamma} \ln\left(\sum_{n=0}^{\infty} e^{-n\gamma}\right) = -h\nu \, \frac{d}{d\gamma} \ln\left(\frac{1}{1-e^{-\gamma}}\right) ,$$

where the last step follows from summing the geometric series (here $e^{-\gamma} < 1$):

$$\sum_{n=0}^{\infty} (e^{-\gamma})^n = \frac{1}{1-e^{-\gamma}} .$$

After carrying out the derivative in γ, we find

$$\langle\text{energy}\rangle = \frac{h\nu}{e^{h\nu/k_B T} - 1} ,$$

and therefore

$$u(\nu, T)\, d\nu = \frac{1}{V} \langle\text{energy}\rangle \times (\text{number of modes in } d\nu) = \frac{8\pi h}{c^3} \frac{\nu^3}{e^{h\nu/k_B T} - 1} \, d\nu ,$$

the correct black-body radiation formula first derived by Planck. Comparison with observation gives $k_B \approx 1.38 \times 10^{-16}$ erg/K and $h \approx 6.63 \times 10^{-27}$ erg sec. The formula above reproduces the Rayleigh–Jeans law at small $h\nu/(k_B T)$ but predicts an exponential fall-off at large frequency, in agreement with experimental data; see Fig. 1.1. In particular, the total energy density is now finite and is proportional to T^4, since

$$\int_0^{\infty} u(\nu, T)\, d\nu = \frac{8\pi h}{c^3} \left(\frac{k_B T}{h}\right)^4 \overbrace{\int_0^{\infty} \frac{x^3}{e^x - 1}\, dx}^{\pi^4/15} = \frac{8\pi^5}{15} \frac{k_B^4}{h^3 c^3} T^4 ,$$

where in the integral we have introduced the non-dimensional variable $x = h\nu/(k_B T)$. Thus, the successful explanation of the black-body energy spectrum sketched above suggests that light of frequency ν consists of quanta of energy $h\nu$.

Problem 2 Compton Scattering for an Electron in Motion in the Lab Frame

Consider the scattering of monochromatic photons by free electrons (Compton scattering).

1. Assuming that the electron is initially at rest and using energy and momentum conservation, show that the shift in the photon wavelength $\Delta\lambda = \lambda_f^\gamma - \lambda_i^\gamma$ is given by

   $$\Delta\lambda = 2\lambda_e \sin^2\theta_0/2 \qquad \text{with} \qquad \lambda_e = \frac{h}{mc} ,$$

   where m is the electron mass, c is the speed of light, and θ_0 is the angle between the momentum of the scattered photon and the momentum of the incident photon. Determine (under the same assumption) the magnitude and direction of the recoil momentum of the electron as a function of the incident-photon energy E_i^γ and scattering angle θ_0.
2. Assume that the electron has an initial momentum $\mathbf{p}_i$ parallel to the incident-photon momentum $\mathbf{p}_i^\gamma$. Using energy and momentum conservation, show that the wavelength shift is given by

   $$\Delta\lambda = 2\lambda_i^\gamma \, \frac{p_i^\gamma + p_i}{E_i/c - p_i} \sin^2\theta/2 ,$$

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where λ_i^γ is the wavelength of the incident photon, θ is the angle of the scattered photon, and $E_i = c\sqrt{p_i^2 + (mc)^2}$ is the initial energy of the electron.

3. Show that the result in part 2 can be derived from the expressions in part 1 when the electron is initially at rest, by a suitable Lorentz transformation.

Solution

Part 1

In the rest frame of the electron, let $\mathbf{p}_i^{\gamma\,\prime}$ and $\mathbf{p}_f^{\gamma\,\prime}$ be the incident- and scattered-photon momenta. Energy and momentum conservation give

$$\mathbf{p}_i^{\gamma\,\prime} = \mathbf{p}_f^{\gamma\,\prime} + \mathbf{p}'_f \,, \qquad E_i^{\gamma\,\prime} + mc^2 = E_f^{\gamma\,\prime} + E'_f \,,$$

where $\mathbf{p}'_f$ and E'_f denote the scattered-electron momentum and energy. Exploiting momentum conservation, we have

$$E_i^{\gamma\,\prime} + mc^2 - E_f^{\gamma\,\prime} = c\sqrt{(mc)^2 + (\mathbf{p}_i^{\gamma\,\prime} - \mathbf{p}_f^{\gamma\,\prime})^2} \,.$$

Squaring both sides and recalling that the photon is massless (and hence $E^\gamma = c\,|\mathbf{p}^\gamma|$), we arrive at

$$2mc^2\,(E_i^{\gamma\,\prime} - E_f^{\gamma\,\prime}) - 2E_i^{\gamma\,\prime}\,E_f^{\gamma\,\prime} = -2E_i^{\gamma\,\prime}\,E_f^{\gamma\,\prime}\,\cos\theta_0 \,,$$

yielding

$$E_f^{\gamma\,\prime} = \frac{E_i^{\gamma\,\prime}}{1 + (E_i^{\gamma\,\prime}/mc^2)(1 - \cos\theta_0)} = \frac{E_i^{\gamma\,\prime}}{1 + 2(E_i^{\gamma\,\prime}/mc^2)\sin^2(\theta_0/2)} \,,$$

where θ_0 is the photon scattering angle (in the electron rest frame). Recalling that for a photon

$$E^\gamma = \hbar\omega^\gamma = \hbar c|\mathbf{k}^\gamma| = \frac{2\pi\hbar c}{\lambda^\gamma} = \frac{hc}{\lambda^\gamma} \,,$$

the relationship between the initial and final photon energies can be cast in terms of the initial and final wavelengths as

$$\frac{hc}{\lambda_f^{\gamma\prime}} = \frac{hc}{\lambda_i^{\gamma\prime}}\,\frac{1}{1 + 2(hc/(\lambda_i^{\gamma\prime}mc^2))\sin^2(\theta_0/2)} \implies \lambda_f^{\gamma\prime} = \lambda_i^{\gamma\prime} + 2\underbrace{\frac{h}{mc}}_{\lambda_e}\sin^2(\theta_0/2) \,,$$

the required expression for the wavelength shift $\Delta\lambda' = \lambda_f^{\gamma\prime} - \lambda_i^{\gamma\prime}$ is

$$\Delta\lambda' = 2\lambda_e\sin^2(\theta_0/2) \,,$$

where λ_e is the Compton wavelength of the electron. In order to determine the electron scattering angle in the initial electron rest frame, we use momentum conservation to obtain

$$p_i^{\gamma\prime} = p_f^{\gamma\prime}\,\cos\theta_0 + p'_f\,\cos\theta_0^e \,, \qquad 0 = p_f^{\gamma\prime}\,\sin\theta_0 + p'_f\,\sin\theta_0^e \,,$$

where θ_0^e is the electron scattering angle. We have

$$p'_f\,\sin\theta_0^e = -p_f^{\gamma\prime}\,\sin\theta_0 \,, \qquad p'_f\,\cos\theta_0^e = p_i^{\gamma\prime} - p_f^{\gamma\prime}\,\cos\theta_0 \,,$$

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yielding

$$\tan\theta_0^e = -\frac{p_f^{\gamma\prime}\sin\theta_0}{p_i^{\gamma\prime} - p_f^{\gamma\prime}\cos\theta_0} = -\frac{\sin\theta_0}{E_i^{\gamma\prime}/E_f^{\gamma\prime} - \cos\theta_0} \ .$$

Using

$$E_i^{\gamma\prime}/E_f^{\gamma\prime} = 1 + (E_i^{\gamma\prime}/mc^2)(1-\cos\theta_0) \ ,$$

we arrive at

$$\tan\theta_0^e = -\frac{\sin\theta_0}{1 + (E_i^{\gamma\prime}/mc^2)(1-\cos\theta_0) - \cos\theta_0} = -\frac{\sin\theta_0}{1-\cos\theta_0}\,\frac{1}{1+E_i^{\gamma\prime}/mc^2} = -\frac{\cot(\theta_0/2)}{1+E_i^{\gamma\prime}/mc^2} \ .$$

To determine the magnitude of the electron's final momentum, we square both sides of the energy-conservation relation to find

$$\underbrace{c^2(p_f'^2 + m^2c^2)}_{E_f'^2} = \underbrace{E_i^{\gamma\prime 2} + E_f^{\gamma\prime 2} + m^2c^4 + 2mc^2(E_i^{\gamma\prime} - E_f^{\gamma\prime}) - 2E_i^{\gamma\prime}E_f^{\gamma\prime}}_{(E_i^{\gamma\prime}+mc^2-E_f^{\gamma\prime})^2} \ ,$$

which reduces to

$$c^2 p_f'^2 = (E_i^{\gamma\prime} - E_f^{\gamma\prime})(E_i^{\gamma\prime} - E_f^{\gamma\prime} + 2mc^2) \ .$$

Inserting into $p_f'^2$ the expression for the difference between the initial and final photon energies,

$$E_i^{\gamma\prime} - E_f^{\gamma\prime} = E_i^{\gamma\prime}\,\frac{2(E_i^{\gamma\prime}/mc^2)\sin^2(\theta_0/2)}{1 + 2(E_i^{\gamma\prime}/mc^2)\sin^2(\theta_0/2)} \ ,$$

yields the required relation between the magnitude of the electron's final momentum and the photon's initial energy and final scattering angle.

Part 2

We call the frame in which the electron has initial momentum $\mathbf{p}_i$ the lab frame. By assumption $\mathbf{p}_i$ is parallel to $\mathbf{p}_i^\gamma$. We will denote the momenta and energies of the electron and photons by unprimed symbols, so $\mathbf{p}_i^\gamma$, E_i^γ and $\mathbf{p}_f^\gamma$, E_f^γ are the initial and final photon momenta and energies and $\mathbf{p}_i$, E_f and $\mathbf{p}_f$, E_f are the initial and final electron momenta and energies, respectively. Energy and momentum conservation in this frame read

$$\mathbf{p}_i^\gamma + \mathbf{p}_i = \mathbf{p}_f^\gamma + \mathbf{p}_f \ , \qquad E_i^\gamma + E_i = E_f^\gamma + E_f \ .$$

These relations imply

$$E_i + E_i^\gamma - E_f^\gamma = c\sqrt{(\mathbf{p}_i + \mathbf{p}_i^\gamma - \mathbf{p}_f^\gamma)^2 + (mc)^2} \ ,$$

and squaring both sides yields

$$E_i(E_i^\gamma - E_f^\gamma) - E_i^\gamma E_f^\gamma = cp_iE_i^\gamma - cp_iE_f^\gamma\cos\theta - E_i^\gamma E_f^\gamma\cos\theta \ ,$$

where we have used the fact that $\mathbf{p}_i$ and $\mathbf{p}_i^\gamma$ are parallel. Rearranging terms, we find

$$E_i^\gamma(E_i - cp_i) = E_f^\gamma(E_i + E_i^\gamma) - E_f^\gamma(E_i^\gamma + cp_i)\cos\theta \ ,$$

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which can be further simplified by using the identity $\cos\theta = 1 - 2\sin^2(\theta/2)$ to obtain

$$E_i^\gamma(E_i - cp_i) = \underbrace{E_f^\gamma(E_i + E_i^\gamma) - E_f^\gamma(E_i^\gamma + cp_i)}_{E_f^\gamma(E_i - cp_i)} + 2E_f^\gamma(E_i^\gamma + cp_i)\sin^2(\theta/2)\,,$$

or, after dividing both sides by $E_i - c\,p_i$,

$$E_i^\gamma = E_f^\gamma + 2E_f^\gamma \frac{E_i^\gamma + cp_i}{E_i - cp_i}\sin^2(\theta/2)\,.$$

In terms of photon wavelengths, the above expression is written as

$$\frac{hc}{\lambda_i^\gamma} = \frac{hc}{\lambda_f^\gamma} + 2\,\frac{hc}{\lambda_f^\gamma}\,\frac{p_i^\gamma + p_i}{E_i/c - p_i}\sin^2(\theta/2) \implies \lambda_f^\gamma = \lambda_i^\gamma + 2\lambda_i^\gamma\,\frac{p_i^\gamma + p_i}{E_i/c - p_i}\sin^2(\theta/2)\,,$$

resulting in a wavelength shift given by

$$\Delta\lambda = 2\lambda_i^\gamma\,\frac{p_i^\gamma + p_i}{E_i/c - p_i}\sin^2(\theta/2)\,.$$

Part 3

Another (instructive) way to solve the problem in Part 2 is to work in the electron's initial rest frame, and then transform back to the lab frame, in which the electron has initial momentum $\mathbf{p}_i$ (parallel to the initial photon momentum $\mathbf{p}_i^\gamma$) and energy E_i. The energy of the scattered photon in the laboratory frame follows from the Lorentz transformation relation:

$$E_f^\gamma = \gamma(E_f^{\gamma\,\prime} + \beta c p_{f,x}^{\gamma\,\prime}) = \gamma E_f^{\gamma\,\prime}(1 + \beta\cos\theta_0),$$

where $\beta\,\hat{\mathbf{x}}$ with $\beta = cp_i/E_i$ is the velocity of the electron in the lab frame, and $\gamma = 1/\sqrt{1-\beta^2}$. By substituting for $E_f^{\gamma\prime}$ the expression found in part 1, we obtain

$$E_f^\gamma = \gamma\,\frac{E_i^{\gamma\,\prime}(1 + \beta\cos\theta_0)}{1 + (E_i^{\gamma\,\prime}/mc^2)(1 - \cos\theta_0)}\,.$$

We need to express the photon energy $E_i^{\gamma\prime}$ and scattered photon angle θ_0 in terms of the corresponding lab frame quantities. The energy of the initial photon in the electron's rest frame is related to its energy in the lab frame by a Lorentz transformation:

$$E_i^{\gamma\,\prime} = \gamma(E_i^\gamma - \beta c\,p_{i,x}^\gamma) = \gamma E_i^\gamma(1 - \beta),$$

where the momentum of the initial photon is along the $\hat{\mathbf{x}}$-direction, and hence $p_{i,x}^\gamma = p_i^\gamma$. The Lorentz transformation also gives

$$p_{f,x}^{\gamma\prime} = \gamma(p_{f,x}^\gamma - \beta E_f^\gamma/c)\,, \qquad p_{f,y}^{\gamma\prime} = p_{f,y}^\gamma\,,$$

which implies that

$$\tan\theta_0 = \frac{p_{f,y}^{\gamma\,\prime}}{p_{f,x}^{\gamma\,\prime}} = \frac{p_{f,y}^\gamma}{\gamma(p_{f,x}^\gamma - \beta E_f^\gamma/c)} = \frac{\sin\theta}{\gamma(\cos\theta - \beta)}\,,$$

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where θ is the angle of the scattered photon in the lab frame. Making use of the identity $\cos\theta_0 = 1/\sqrt{1+\tan^2\theta_0}$, we find

$$\cos\theta_0 = \frac{1}{\sqrt{1+\sin^2\theta/[\gamma^2(\cos\theta-\beta)^2]}} = \frac{\gamma(\cos\theta-\beta)}{\sqrt{\gamma^2(\cos\theta-\beta)^2+\sin^2\theta}}$$
$$= \frac{\cos\theta-\beta}{\sqrt{\cos^2\theta+\beta^2-2\beta\cos\theta+(1-\beta^2)\sin^2\theta}} = \frac{\cos\theta-\beta}{1-\beta\cos\theta},$$

from which we have the following relations:

$$1-\cos\theta_0 = (1+\beta)\,\frac{1-\cos\theta}{1-\beta\cos\theta}, \qquad 1+\beta\cos\theta_0 = \frac{1-\beta^2}{1-\beta\cos\theta} = \frac{1/\gamma^2}{1-\beta\cos\theta}.$$

We insert all these relations into the expression for E_f^γ found above to obtain

$$E_f^\gamma = \frac{\gamma^2 E_i^\gamma(1-\beta)/[\gamma^2(1-\beta\cos\theta)]}{1+\gamma(E_i^\gamma/mc^2)\underbrace{(1-\beta)(1+\beta)}_{1/\gamma^2}(1-\cos\theta)/(1-\beta\cos\theta)} = E_i^\gamma\,\frac{(1-\beta)/(1-\beta\cos\theta)}{1+(E_i^\gamma/\gamma mc^2)(1-\cos\theta)/(1-\beta\cos\theta)}.$$

Recalling that $\beta = cp_i/E_i$ and $E_i = \gamma mc^2$, we finally arrive at

$$E_f^\gamma = E_i^\gamma\,\frac{1-\beta}{1-\beta\cos\theta+(E_i^\gamma/E_i)(1-\cos\theta)} = E_i^\gamma\,\frac{E_i-cp_i}{E_i-cp_i\cos\theta+E_i^\gamma(1-\cos\theta)},$$

which can be simplified by expressing $\cos\theta$ as $1-2\sin^2(\theta/2)$:

$$E_f^\gamma = E_i^\gamma\,\frac{E_i-cp_i}{E_i-cp_i+2\sin^2(\theta/2)\,(E_i^\gamma+cp_i)} = \frac{E_i^\gamma}{1+2\sin^2(\theta/2)\,(E_i^\gamma+cp_i)/(E_i-cp_i)}.$$

In terms of wavelengths this gives

$$\lambda_f^\gamma = \lambda_i^\gamma\left[1+2\sin^2(\theta/2)\,\frac{p_i^\gamma+p_i}{E_i/c-p_i}\right],$$

and the wavelength shift is, of course, identical to that found in part 2 above.

Problem 3 The Thomson Model of the Atom and Rutherford's Experiment

After the discovery of the electron by Thomson in 1897, it was believed that "atoms were like puddings, with negatively charged electrons stuck in like raisins in a smooth background of positive charge" (S. Weinberg). This picture was drastically changed by experiments performed by Rutherford and collaborators, who scattered α particles (^{4}He nuclei, which, as we now know, consist of two protons and two neutrons bound together by the nuclear force, having electric charge $2e$) off a thin foil of gold. Rutherford and collaborators observed α particles scattered at large backward angles. This was totally unexpected, since electrons are much lighter than α particles.

1. Consider a particle of mass M and velocity v hitting a particle of mass m at rest and continuing along the same line with velocity v'. Show that, for a given v, energy and momentum conservation lead to two possible solutions for v'. If a certain condition is satisfied, one of these solutions corresponds to the case in which particle M inverts its direction of motion. What is this condition?

2. Suppose the α particles (which were in fact emitted by a radium source in Rutherford's experiment) have velocity $v \approx 2.1 \times 10^9$ cm/sec, and that the target particles (much heavier than the α particles) have each charge Ze. If the α particles and target particles interact via the Coulomb repulsion, what is the distance of closest approach? Show that this distance is of the order $3\,Z \times 10^{-14}$ cm, and therefore (even for $Z \approx 100$) it is much smaller than atomic radii.

Solution

Part 1

Energy and momentum conservation require

$$\frac{Mv^2}{2} = \frac{Mv'^2}{2} + \frac{mu^2}{2}\,, \qquad Mv = Mv' + mu\,,$$

where, as assumed in the problem, the particle of mass M proceeds after the collision along the same trajectory as it followed before the collision. Replacing u with $M(v-v')/m$ in the energy-conservation relation leads to an equation for v'/v:

$$\left(1 + \frac{M}{m}\right)\left(\frac{v'}{v}\right)^2 - 2\,\frac{M}{m}\frac{v'}{v} - 1 + \frac{M}{m} = 0\,,$$

which has the solutions

$$v' = v\,, \qquad v' = -\frac{m-M}{m+M}\,v\,.$$

The first solution ($v' = v$) says that the particle continues along its trajectory undisturbed, which is unphysical. However, the second solution says that if $m > M$ the particle inverts its trajectory, since in that case $v' < 0$.

Part 2

At the distance of closest approach, the kinetic energy of the α particle must have been converted into potential energy (we are neglecting here the recoil energy of the target particle, that is, we are assuming $m \gg M$),

$$\frac{Mv^2}{2} = \frac{(Ze)(2e)}{r_0} \implies r_0 = \frac{4Ze^2}{Mv^2}\,.$$

We have

$$e^2 \approx 2.3 \times 10^{-19}\ \text{g cm}^3/\text{sec}^2\,, \qquad v \approx 2.1 \times 10^9\ \text{cm/sec}\,, \qquad M \approx 6.6 \times 10^{-24}\ \text{g}\,,$$

where we have expressed e^2 as $\alpha\hbar c$ and α is the (non-dimensional) fine-structure constant having the approximate value $\approx 1/137$ and have used $\hbar \approx 1.05 \times 10^{-27}$ g cm^2/sec and $c = 3.00 \times 10^{10}$ cm/sec. For the mass of the ^{4}He nucleus we have used $Mc^2 = 2(m_p + m_n)c^2 - 28.3$ MeV ≈ 3727 MeV. Here 28.3 MeV is the nuclear binding energy of ^{4}He, and MeV/c$^2 \approx 1.78 \times 10^{-27}$ g. We obtain

$$r_0 \approx 3Z \times 10^{-14}\ \text{cm}\,,$$

which is much smaller than the size of the atom, of the order of 10^{-8} cm.

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Problem 4 The Stability Problem for the Rutherford Model of the Atom

Consider the Rutherford model of the atom: an electron of electric charge $-e$ orbiting a point-like nucleus (much heavier, and hence effectively at rest) of electric charge Ze in a circular orbit of radius R. Knowing that the electron radiates energy away at a rate $dE(t)/dt$, given by

$$\frac{dE(t)}{dt} = -\frac{2}{3}\,\frac{e^2\,|\mathbf{a}(t)|^2}{c^3}\,,$$

where $\mathbf{a}(t)$ is the electron's acceleration and c is the speed of light, show that it will take a time

$$\tau = \frac{m^2c^3}{Ze^4}\,\frac{R^3}{4}\,,$$

for the electron to spiral into the nucleus. Assume that τ is much larger than the revolution period. By taking $Z=1$ and $R \approx 10^{-8}$ cm, as is appropriate for the hydrogen atom, justify this assumption *a posteriori* by comparing τ with the revolution period.

Solution

The electron energy is given by

$$E = \frac{mv^2}{2} - \frac{Ze^2}{r}\,.$$

It is assumed that the electron is in a circular orbit and that the energy lost by emission of radiation per revolution is tiny relative to E. The electron is subject to a centripetal acceleration whose magnitude is given by $a = v^2/r$, where r is the radius of the orbit, so that

$$ma = \frac{Ze^2}{r^2} \implies v^2 = \frac{Ze^2}{mr}\,,$$

and hence

$$E = -\frac{Ze^2}{2r}\,.$$

The radius does change with time, albeit very slowly, corresponding to the loss of energy:

$$\frac{dE}{dt} = \frac{d}{dt}\left(-\frac{Ze^2}{2r}\right) = \frac{Ze^2}{2r^2}\,\frac{dr}{dt} = -\frac{2}{3}\,\frac{e^2a^2}{c^3} = -\frac{2e^2}{3c^3}\left(\frac{Ze^2}{mr^2}\right)^2\,,$$

which leads to

$$\frac{dr}{dt} = -\frac{4}{3}\,\frac{Ze^4}{m^2c^3r^2} \qquad \text{or} \qquad dt = -\frac{3}{4}\,\frac{m^2c^3}{Ze^4}\,r^2\,dr\,.$$

At time $t=0$ the electron is in an orbit of radius $r(0)=R$, while at time τ the electron has "fallen into the nucleus", and so $r(\tau)=0$; therefore, we find by integrating above the differential equation,

$$\int_0^\tau dt = -\frac{3}{4}\,\frac{m^2c^3}{Ze^4}\int_R^0 dr\,r^2 \implies \tau = \frac{m^2c^3}{Ze^4}\,\frac{R^3}{4}\,.$$

We take

$$m \approx 9.1\times10^{-28}\ \text{g}\,, \qquad c = 3.0\times10^{10}\ \text{cm/sec}\,, \qquad e^2 \approx 2.3\times10^{-19}\ \text{g cm}^3/\text{sec}^2\,,$$

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and, for the hydrogen atom, $Z = 1$ and $R \approx 10^{-8}$ cm, and so we find $\tau \approx 10^{-10}$ sec, while the revolution period is

$$T = 2\pi \frac{R}{v} = 2\pi R \left(\frac{mR}{Ze^2}\right)^{1/2} \approx 4 \times 10^{-16} \text{ sec} ,$$

giving $T \ll \tau$ as assumed.

Problem 5 Bohr's Calculation of the Energy Spectrum of the Hydrogen Atom

In order to solve the stability problem, Niels Bohr proposed in 1913 that the atom can exist only in certain states having energies $E_1 < E_2 < \cdots$, that is, atomic energies are quantized. To obtain these energies, Bohr assumed that the angular momentum of an electron of mass m and electric charge $-e$ in a *stable circular orbit* of radius r around a nucleus of electric charge Ze is an integer multiple n of the Planck constant $\hbar = h/(2\pi)$. Following Bohr, calculate the energies E_n.

Solution

The magnitude of the angular momentum of the electron in a circular orbit of radius r is given by mvr, where v is the magnitude of the velocity, and according to Bohr's hypothesis

$$mvr = n\hbar .$$

The attractive Coulomb force acting on the electron is responsible for its centripetal acceleration, which reads (in magnitude)

$$\frac{v^2}{r} = \frac{Ze^2}{mr^2} \implies r = \frac{Ze^2}{mv^2} .$$

When combined with the quantization condition, this leads to

$$v = \frac{Ze^2}{n\hbar} ,$$

and hence to the energy levels, given by (after substituting for r and v the expressions above)

$$E = \frac{mv^2}{2} - \frac{Ze^2}{r} = -\frac{mv^2}{2} \implies E_n = -\frac{Z^2e^4m}{2n^2\hbar^2} = -\frac{(Z\alpha)^2mc^2}{2n^2} ,$$

which turns out to give the (correct!) result obtained in Schrödinger's wave mechanics.

Problem 6 The Bohr–Sommerfeld Quantization Rule and the Harmonic Oscillator Energy Spectrum

In the old quantum theory, one assumes that the particles follow the laws of classical mechanics but one postulates further that, of all the possible solutions of the equations of motion, one must retain only those which satisfy certain *ad hoc* quantization rules. One therefore selects a discontinuous family of motions; these are, by hypothesis, the only motions which are realized in nature. The discontinuous sequence of energy values thus obtained constitutes the spectrum of quantized energy levels.

For a one-dimensional periodic motion, the quantization rule, known as the Bohr–Sommerfeld quantization rule, is

$$\oint_E dq\, p = nh \qquad n = 1, 2, \ldots\,,$$

where h is Planck's constant – recall that $\hbar = h/(2\pi)$ – and the symbol $\oint_E$ means that one must integrate over a complete period of the motion corresponding to the energy E. Here q and p are the position and momentum variables, respectively. The integral is known as the action integral. Apply this rule to the case of the one-dimensional harmonic oscillator, for which

$$E = \frac{p^2}{2m} + \frac{m\omega^2}{2}\, q^2\,.$$

Calculate the energy, period, and amplitude of the quantized trajectories.

Solution

For a fixed energy E, the momentum p is given by

$$p = \sqrt{2mE\left(1 - \frac{m\omega^2}{2E}\, q^2\right)}\,,$$

and it vanishes at the endpoints $\pm\, q_0$, where

$$q_0 = \sqrt{\frac{2E}{m\omega^2}}\,.$$

The Bohr–Sommerfeld rule requires that

$$2\int_{-q_0}^{q_0} dq\, \sqrt{2mE\left(1 - \frac{q^2}{q_0^2}\right)} = nh\,,$$

where the factor 2 in front of the integral accounts for the fact that over a full period the particle goes from $-q_0$ to q_0 and back to $-q_0$. Substituting $x = q/q_0$, the left-hand side can written as follows:

$$\text{l.h.s.} = 2\,\sqrt{2mE}\, q_0 \underbrace{\int_{-1}^{1} dx\, \sqrt{1 - x^2}}_{\pi/2} \implies \text{l.h.s.} = 2\pi\, \frac{E}{\omega}\,,$$

after substituting for q_0. The Bohr–Sommerfeld gives

$$2\pi\, \frac{E}{\omega} = nh \implies E_n = n\hbar\omega \qquad \text{with } \; n = 1, 2, \ldots$$

Note that the exact quantum result is $E_n = (n + 1/2)\hbar\omega$ with $n = 0, 1, 2, \ldots$ The period of the harmonic oscillator is $2\pi/\omega$, while its amplitude A_n is simply given by q_0 and is therefore quantized,

$$A_n = \sqrt{\frac{2\hbar}{m\omega}}\, \sqrt{n}\,.$$

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Problem 7 An Application of the Bohr–Sommerfeld Quantization Rule to the Hydrogen Atom

Quantize the *circular* electronic orbits of the hydrogen atom by applying the Bohr–Sommerfeld rule introduced in the previous problem. Determine the energy, period, and radius of the quantized orbits. Calculate specifically the numerical values of the energy, period, and radius of the lowest orbit. Use $mc^2 \approx 0.51 \times 10^6$ eV and $\hbar c/e^2 \approx 137$.

Solution

The energy of a hydrogen-like atom is given by

$$E = \frac{p^2}{2m} - \frac{Ze^2}{r} ,$$

where m and $-e$ are the electron mass and charge; we assume that the nucleus of charge Ze is fixed at the origin (we will neglect reduced-mass corrections). In a circular orbit the centripetal acceleration of the electron is provided by the attractive Coulomb force, and hence

$$m\,\frac{v^2}{r} = \frac{Ze^2}{r^2} \implies \frac{p^2}{m} = \frac{Ze^2}{r} ,$$

where r is the radius of the circular orbit; the magnitude p of the electron momentum is constant (but not its direction, of course). The momentum corresponding to a given energy for such an orbit is then given by

$$E = \frac{p^2}{2m} - \frac{p^2}{m} = -\frac{p^2}{2m} \implies p = \sqrt{2m|E|} ,$$

and the action integral for such an orbit follows from

$$\oint_E dq\, p = \oint_E d\mathbf{s} \cdot \mathbf{p} = p \int_0^{2\pi} r d\theta = 2\pi r p = 2\pi r \sqrt{2m|E|} .$$

For a given E, the radius of the circular orbit is given by

$$E = \frac{p^2}{2m} - \frac{Ze^2}{r} = \frac{Ze^2}{2r} - \frac{Ze^2}{r} = -\frac{Ze^2}{2r} \implies r = \frac{Ze^2}{2|E|} .$$

Inserting this expression into the action–integral result and imposing the Bohr–Sommerfeld rule yields

$$2\pi \frac{Ze^2}{2|E|} \sqrt{2m|E|} = nh \implies E_n = -\frac{m}{2n^2} \frac{Z^2 e^4}{\hbar^2} = -\frac{(Z\alpha)^2}{2n^2} mc^2 ,$$

where we have introduced the fine-structure constant $\alpha = e^2/(\hbar c) \approx 1/137$ and $mc^2 \approx 0.51$ MeV is the electron rest mass. The result above for E_n turns out to agree with that obtained in Schrödinger's wave mechanics. The radii of these circular orbits are quantized,

$$r_n = \frac{Ze^2}{2|E_n|} = \frac{e^2}{Z\alpha^2 mc^2} n^2 = \frac{1}{Z\alpha} \frac{\hbar}{mc} n^2 = \frac{a_0}{Z} n^2 ,$$

where we have expressed e^2 in terms of the fine-structure constant as $\alpha\hbar c$ and have introduced the Bohr radius a_0:

$$a_0 = \frac{\hbar}{\alpha mc} \approx 0.53 \times 10^{-8} \text{ cm} .$$

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The periods of the orbits also turn out to be quantized,

$$T_n = 2\pi \frac{r_n}{p_n/m} \implies T_n = 2\pi \frac{n^2 a_0}{Z} \sqrt{\frac{m}{2|E_n|}} = 2\pi \frac{n^3}{Z^2\alpha} \frac{a_0}{c} .$$

For the hydrogen atom having $Z = 1$ and for the most bound orbit, corresponding to $n = 1$, we find

$$E_1 = -13.6 \text{ eV} , \qquad r_1 = 0.53 \times 10^{-8} \text{ cm} , \qquad T_1 = 1.5 \times 10^{-16} \text{ sec} .$$

Problem 8 Heat Capacity of Solids

In addition to the failures in explaining the black-body radiation spectrum, the photoelectric effect, and the stability of atoms and spectral lines, classical physics could not explain the heat capacity of a solid.

1. Assume that a solid of volume V with N atoms (or molecules) can be modeled as a set of $3N$ independent one-dimensional harmonic oscillators of frequency ν_0 (that is, all oscillators have the same frequency ν_0). Making use of the equipartition theorem, calculate the total average energy E of the solid at temperature T and derive the Dulong–Petit law for the heat capacity (at constant volume),

$$c_V = \left(\frac{\partial E}{\partial T}\right)_V = 3N k_B ,$$

where k_B is Boltzmann's constant.

2. The observed heat capacity of a solid is not in fact a constant independent of T but rather vanishes as T^3 at low temperature and only approaches the classical prediction (the Dulong–Petit law) at high temperatures. Einstein (1907) proposed that the energy of each harmonic oscillator is quantized and that its average energy at temperature T is given as follows:

$$\text{average energy} = \frac{h\nu_0}{e^{h\nu_0/k_B T} - 1} .$$

Show that the heat capacity is now found to be

$$c_V = 3Nk_B \frac{x_0^2 \, e^{x_0}}{(e^{x_0} - 1)^2} , \qquad x_0 = \frac{h\nu_0}{k_B T} .$$

Does c_V vanish as $T \longrightarrow 0$? What happens at high temperature?

3. Einstein's theory predicts that c_V vanishes exponentially at low temperature, a result that is at variance with experimental observations. A more realistic model of a solid is that it consists of $3N$ independent harmonic oscillators (normal modes) with a distribution in frequency $g(\nu)$ given by

$$g(\nu) = 4\pi \frac{V}{v_S^3} \nu^2 ,$$

where v_S is the sound velocity in the solid, such that

$$\text{number of modes} = \int_0^{\nu_{\max}} d\nu \, g(\nu) = 3N .$$

This condition fixes $\nu_{\max}$ as a function of the density N/V. Introduce the parameter T_D (the Debye temperature), defined as

$$T_D = \frac{h\nu_{\max}}{k_B} ,$$

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and show that the total average energy at temperature T is given by

$$E = 9Nh\nu_{\max}\left(\frac{T}{T_D}\right)^4 \int_0^{T_D/T} dx\, \frac{x^3}{e^x - 1} ,$$

and that the constant-volume heat capacity is proportional to T^3 for low T, in agreement with experiment. Show that it also satisfies the Dulong–Petit law at high temperatures.

Solution

Part 1

Each oscillator contributes $k_B T$ to the total average energy E of the solid held at temperature T, and, since there are $3N$ oscillators, this total energy is simply $3Nk_BT$, which immediately yields the Dulong–Petit law given in the text of the problem.

Part 2

Einstein's theory gives for the total average energy

$$E = 3N\,\frac{h\nu_0}{e^{h\nu_0/k_BT} - 1} = 3Nk_BT\,\underbrace{\frac{x_0}{e^{x_0} - 1}}_{f(x_0)} ,$$

and the heat capacity at constant volume is then as follows:

$$c_V = \left(\frac{\partial E}{\partial T}\right)_V = 3Nk_B f(x_0) + 3Nk_BT\,\frac{\partial f(x_0)}{\partial x_0}\,\frac{\partial x_0}{\partial T}$$
$$= 3Nk_B\,\frac{x_0}{e^{x_0} - 1} - 3Nk_BT\left[\frac{1}{e^{x_0} - 1} - \frac{x_0\, e^{x_0}}{(e^{x_0} - 1)^2}\right]\frac{x_0}{T} = 3Nk_B\,\frac{x_0^2\, e^{x_0}}{(e^{x_0} - 1)^2} .$$

In the limit of low T, x_0 becomes large and $c_V \approx 3Nk_Bx_0^2\, e^{-x_0}$ vanishes exponentially. In the high-T limit, we have $x_0 \longrightarrow 0$, and hence

$$c_V = 3Nk_B\,\frac{x_0^2(1 + x_0 + \cdots)}{(x_0 + x_0^2/2 + \cdots)^2} = 3Nk_B\,\frac{1 + x_0 + \cdots}{(1 + x_0/2 + \cdots)^2} \approx 3Nk_B ,$$

and the Dulong–Petit law is reproduced in this limit up to corrections proportional to x_0^2.

Part 3

We have

$$\int_0^{\nu_{\max}} d\nu\, g(\nu) = 3N \qquad \text{or} \qquad \frac{4\pi}{3}\,\frac{V}{v_S^3}\,\nu_{\max}^3 = 3N \Longrightarrow \nu_{\max} = v_S\left(\frac{9}{4\pi}\,\rho\right)^{1/3} .$$

The total average energy follows from

$$E = \int_0^{\nu_{\max}} d\nu\, g(\nu)\,\frac{h\nu}{e^{h\nu/k_BT} - 1} = 4\pi V\,\frac{h}{v_S^3}\int_0^{\nu_{\max}} d\nu\,\frac{\nu^3}{e^{h\nu/k_BT} - 1} ,$$

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which, after introducing the integration variable $x = h\nu/(k_B T)$, can also be expressed as

$$E = 4\pi V \frac{h}{v_S^3} \left(\frac{k_B T}{h}\right)^4 \int_0^{T_D/T} dx \, \frac{x^3}{e^x - 1} = 4\pi V \frac{h}{v_S^3} \nu_{\max}^4 \left(\frac{T}{T_D}\right)^4 \int_0^{T_D/T} dx \, \frac{x^3}{e^x - 1}$$

or, using the relation $(\nu_{\max}/v_S)^3 = (9/4\pi)\rho$,

$$E = 9Nh\nu_{\max} \left(\frac{T}{T_D}\right)^4 \int_0^{T_D/T} dx \, \frac{x^3}{e^x - 1} \, .$$

In the limit of low T, the ratio $T_D/T \longrightarrow \infty$, and hence we have

$$E \approx 9Nh\nu_{\max} \left(\frac{T}{T_D}\right)^4 \underbrace{\int_0^{\infty} dx \, \frac{x^3}{e^x - 1}}_{T \text{ independent}} \implies c_V \propto T^3 \, .$$

By contrast, at high T we have $T_D/T \longrightarrow 0$, and the integral can be approximated as

$$\int_0^{T_D/T} dx \, \frac{x^3}{e^x - 1} \approx \int_0^{T_D/T} dx \, x^2 = \frac{1}{3} \left(\frac{T}{T_D}\right)^3 \, ,$$

where we have expanded the integrand for small x, since $x \ll 1$ in the range $0 \leq x \leq T_D/T$. Thus, we find for E,

$$E \approx 3Nh\nu_{\max} \left(\frac{T}{T_D}\right)^4 \left(\frac{T_D}{T}\right)^3 = 3N \frac{h\nu_{\max}}{T_D} T = 3Nk_B T \implies c_V = 3Nk_B \, ,$$

in agreement with the Dulong–Petit law.