Notes on wave-particle duality

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These notes are intended as supporting material for my video *This is how the wave-particle duality of light was discovered* [1].

Einstein-Gibbs fluctuation formula

In his 1904 article *On the General Molecular Theory of Heat* [2], Einstein presents a new way of estimating Boltzmann constant and the argument for characterizing the stability of a thermodynamics system using the second moment (variance) of the thermodynamical distribution of energies. This quantity called the *fluctuation* is denoted by $\langle\epsilon^2\rangle$ and explicitly defined as

$$\langle\epsilon^2\rangle \equiv \langle E^2\rangle - \langle E\rangle^2. \tag{1}$$

We can explicitly write the two averages of a thermodynamic system at temperature T in the form

$$\langle E^2\rangle = \frac{\displaystyle\int_0^\infty E^2\, e^{-\beta E}\omega(E)\, dE}{\displaystyle\int_0^\infty e^{-\beta E}\omega(E)\, dE}, \quad \langle E\rangle = \frac{\displaystyle\int_0^\infty E\, e^{-\beta E}\omega(E)\, dE}{\displaystyle\int_0^\infty e^{-\beta E}\omega(E)\, dE}, \tag{2}$$

where $e^{-\beta E}$ is the Boltzmann distribution, $\beta = 1/kT$, and $\omega(E)$ is the density of states with energy E. Notice that these two expression are the definitions of $\langle E^2\rangle$ and $\langle E\rangle$; nonetheless, as presented below, there is no need to evaluate these integrals.

Let us consider the average energy $\langle E\rangle$ defined in (2) as the ratio of two functions of the temperature via β in the form

$$\langle E\rangle = \frac{f(\beta)}{g(\beta)}, \tag{3}$$

and calculate the derivative of the average energy with respect to β, which using the rules of the derivative becomes

$$\frac{\partial\langle E\rangle}{\partial\beta} = \frac{1}{g}\frac{\partial f}{\partial\beta} - \frac{f}{g^2}\frac{\partial g}{\partial\beta}. \tag{4}$$

Using the explicit forms of the numerator and denominator in (2) to identify the function f and g we get

$$
\begin{aligned}
\frac{\partial\langle E\rangle}{\partial\beta} &= \frac{\displaystyle\int_0^\infty (-E^2)\, e^{-\beta E}\omega(E)\, dE}{\displaystyle\int_0^\infty e^{-\beta E}\omega(E)\, dE} - \frac{\displaystyle\int_0^\infty E\, e^{-\beta E}\omega(E)\, dE \int_0^\infty (-E)\, e^{-\beta E}\omega(E)\, dE}{\left(\displaystyle\int_0^\infty e^{-\beta E}\omega(E)\, dE\right)^2} \\
&= -\frac{\displaystyle\int_0^\infty E^2\, e^{-\beta E}\omega(E)\, dE}{\displaystyle\int_0^\infty e^{-\beta E}\omega(E)\, dE} + \left(\frac{\displaystyle\int_0^\infty E\, e^{-\beta E}\omega(E)\, dE}{\displaystyle\int_0^\infty e^{-\beta E}\omega(E)\, dE}\right)^2 \\
&= -\langle E^2\rangle + \langle E\rangle^2. \qquad (5)
\end{aligned}
$$

The identification of the two terms defining the fluctuation (1) allows writing

$$\langle\epsilon^2\rangle = -\frac{\partial\langle E\rangle}{\partial\beta}. \qquad (6)$$

Using the chain rule and the relation between temperature and β, this relation can be written in the form

$$\langle\epsilon^2\rangle = -\frac{\partial T}{\partial\beta}\frac{\partial\langle E\rangle}{\partial T} = kT^2\frac{\partial\langle E\rangle}{\partial T}. \qquad (7)$$

This result is known as the Einstein-Gibbs fluctuation formula.

Wave equation

Let us describe light as a wave. From Maxwell's equations the electric field satisfies the wave equation

$$\frac{1}{c^2}\frac{\partial^2\vec{E}}{\partial t^2} = \nabla^2\vec{E}, \qquad (8)$$

where the electric field $\vec{E}$ is a function of three spatial coordinates and time. We will solve this equation for radiation contained in a cubic box of side L. We will use the method of separation of variables, this is the same presented in my video about solving the neutron diffusion equation for calculating the critical mass of an atomic bomb [3].

Solving the wave equation

We propose a solution for the electric field given by the product of four one-dimensional functions of each coordinate:

$$\vec{E}(t,x,y,z) = \vec{E}_0\, X(x)Y(y)Z(z)T(t), \qquad (9)$$

where $\vec{E}_0$ is a constant amplitude. Plugging this ansatz in the wave equation 8 we get

$$\frac{XYZ}{c^2}\frac{d^2T}{dt^2} = YZT\frac{d^2X}{dx^2} + XZT\frac{d^2Y}{dy^2} + XYT\frac{d^2Z}{dz^2}, \qquad (10)$$

we now divide by $XYZT$ to obtain the following:

$$\frac{1}{c^2 T}\frac{d^2 T}{dt^2} = \frac{1}{X}\frac{d^2 X}{dx^2} + \frac{1}{Y}\frac{d^2 Y}{dy^2} + \frac{1}{Z}\frac{d^2 Z}{dz^2}. \tag{11}$$

Note that each of the four terms in this equation involves a single coordinate so we can introduce the so-called *separation constants*, one for each term. We will denote them by k_0, k_1, k_2, k_3 so that

$$\frac{1}{c^2 T}\frac{d^2 T}{dt^2} = k_0^2 \tag{12}$$

$$\frac{1}{X}\frac{d^2 X}{dx^2} = k_1^2 \tag{13}$$

$$\frac{1}{Y}\frac{d^2 Y}{dy^2} = k_2^2 \tag{14}$$

$$\frac{1}{Z}\frac{d^2 Z}{dz^2} = k_3^2, \tag{15}$$

and now we have transformed a four-dimensional partial differential equation (11) into four one-dimensional ordinary differential equations, that can be easily solved separately.

The equation for the time function can be written in the form

$$\frac{d^2 T}{dt^2} = c^2 k_0^2\, T, \tag{16}$$

which has the form of a harmonic equation, whose solution is a linear combination of sine and cosine functions

$$T(t) = A_t \sin(ck_0\, t) + B_t \cos(ck_0\, t), \tag{17}$$

where A_t and B_t are integration constants to be determined by the boundary conditions. If the electric field vanishes at $t = 0$, then we find that $A_t = 1$ and $B_t = 0$, so that the solution reduces to

$$T(t) = \sin(ck_0\, t). \tag{18}$$

For any wave, the oscillation phase (factor in the sin function) can be written as $2\pi\nu t$, where ν is the wave frequency, from were we find that the separation constant for the time coordinate is

$$k_0 = \frac{2\pi\nu}{c}. \tag{19}$$

The final solution of the time function becomes

$$T(t) = \sin(2\pi\nu t). \tag{20}$$

Let us now solve the equation for the x coordinate (13). Just like the equation for the time coordinate, the equation for the function X can be written in the form

$$\frac{d^2 X}{dx^2} = k_1^2\, X, \tag{21}$$

which has the form of a harmonic equation, whose solution is a linear combination of sine and cosine functions

$$X(x) = A_x \sin(k_1 x) + B_x \cos(k_1 x), \tag{22}$$

where A_x and B_x are integration constants to be determined by the boundary conditions. According to Maxwell's equations, the electric field must vanish at the edges of the box and the solution must satisfy $\vec{E}(t, x = 0, y, z) = 0$ and $\vec{E}(t, x = L, y, z) = 0$. The first condition (at $x = 0$) implies that $A_x = 1$ and $B_x = 0$, whereas the second condition (at $x = L$) implies that the separation constant for the x coordinate is

$$k_1 = \frac{\pi n_1}{L}, \quad n_1 = 1, 2, 3, \ldots \tag{23}$$

The final solution of the function X becomes

$$X(x) = \sin\left(\frac{\pi n_1 x}{L}\right), \quad n_1 = 1, 2, 3, \ldots \tag{24}$$

Since the equations for Y (14) and Z (15) have the same form as the equation for X (13), after replacing k_1 by k_2 and k_3, respectively, then their solutions can be found following the exact steps above. Their respective solutions become

$$Y(y) = \sin\left(\frac{\pi n_2 y}{L}\right), \quad n_2 = 1, 2, 3, \ldots \tag{25}$$

$$Z(z) = \sin\left(\frac{\pi n_3 z}{L}\right), \quad n_3 = 1, 2, 3, \ldots \tag{26}$$

Combining all the individual solutions we finally can write the full solution to the electric field of radiation of frequency ν enclosed in a cubic box of sides L as

$$\vec{E}(t, x, y, z) = \vec{E}_0 \sum_{n_1} \sum_{n_2} \sum_{n_3} \sin\left(\frac{\pi n_1 x}{L}\right) \sin\left(\frac{\pi n_2 y}{L}\right) \sin\left(\frac{\pi n_3 z}{L}\right) \sin(2\pi\nu t), \tag{27}$$

where the sum over the integer labels is included to have the most general solution.

Wave modes

Solving the wave equation was a necessary step to characterize the radiation in the box so we can now determine the number of wave modes. Nonetheless, rather than the solution (27), we only need to make use of the values of each of the separation constants and how they are all related. This can be obtained by replacing (12, 13, 14, and 15) into (11), which gives

$$k_0^2 = k_1^2 + k_2^2 + k_3^2. \tag{28}$$

Replacing the value of each separation constant obtained from the boundary conditions we obtain

$$\left(\frac{2\pi\nu}{c}\right)^2 = \left(\frac{\pi n_1}{L}\right)^2 + \left(\frac{\pi n_2}{L}\right)^2 + \left(\frac{\pi n_3}{L}\right)^2. \tag{29}$$

Rearranging terms and considering the integer labels n_1, n_2, and n_3 as the coordinates in a three-dimensional *label space* we get

$$\left(\frac{2L\nu}{c}\right)^2 = n_1^2 + n_2^2 + n_3^2, \tag{30}$$

which represents a sphere of radius $R = 2L\nu/c$. Since the integer labels only take positive values the whole sphere in the modes-label space is not available but rather only one eighth ($n_1 > 0, n_2 > 0$, and $n_3 > 0$). We can count the number of wave modes M by calculating the volume of of the 1/8 sphere in the form

$$\mathbf{M} = 2 \times \frac{1}{8} \times \frac{4}{3}\pi R^3. \tag{31}$$

The overall factor 2 included here accounts for the fact that for a given frequency ν, the radiation can have two possible polarization modes. Replacing the radius of the sphere (30), the number of modes becomes

$$\mathbf{M} = 2 \times \frac{1}{8} \times \frac{4}{3}\pi \left(\frac{2L\nu}{c}\right)^3 = \frac{8\pi\nu^3 L^3}{3c^3}, \tag{32}$$

where we can write the volume of the box as $V = L^3$. Now we can finally write the number of wave modes M at a given radiation frequency within the range ν and $\nu + \Delta\nu$ in the form

$$M = \frac{d\mathbf{M}}{d\nu}\Delta\nu = \frac{8\pi\nu^2 V \Delta\nu}{c^3}. \tag{33}$$

This is the expression used by Rayleigh and Jeans to express their energy density and the relation used in the video about the wave-particle duality [1].

Comments

These notes will be updated in case that any correction is needed. I will also likely include extra material soon. If you spot any typo or error in the calculation just use the the comments section of the video and report the problem, I will happily fix it here.

References

[1] *This is how the wave-particle duality of light was discovered*, YouTube youtu.be/f7JvywBOGYY

[2] A. Einstein, *On the General Molecular Theory of Heat*, Ann. Phys. 14, 354 (1904). English version via Einstein's Papers Online.

[3] *How to calculate an atomic bomb's critical mass*, youtu.be/DIuoFAW9H3E