The Maxwell demon in the osmotic membrane

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Abstract

The dielectric with index of refraction n is inserted in the Planck blackbody. The spectral formula for photons in such dielectric medium and the equation for the temperature of photons is derived. The new equation is solved for the constant index of refraction. The photon flow initiates the osmotic pressure of he Debye phonons. The dielectric crystal surface works as the osmotic membrane with the Maxwell demonic refrigerator.

Key words: Thermodynamics, blackbody, photons, phonons, dielectric medium, dispersion.

1 Introduction

The Maxwell demon opens the door to allow only the faster than average molecules to flow through to a favored side of the chamber, and only the slower than average molecules to the other side, causing the favored side to gradually heat up while the other side cools down, thus decreasing entropy. In osmosis, the doors are open, but only for particles with physical visa, leading to the asymetrical transport of particles.

The classical osmosis is the spontaneous passage of solvent molecules through a partially permeable membrane separating two solutions of different concentration into a region of higher solute concentration of solute, in order to equalize the solute concentrations on the two sides. Osmosis will stop when the two solutions reach equal concentration and can also be stopped by applying a pressure to the liquid on the stronger solution side of the membrane. The pressure of stopping diffusion is so called the osmotic pressure and it depends only on the concentration of solutions and not on their nature. The physical law which controll the osmotic pressure is so called van't Hoff's equation (published in 1885):

$$p = i\frac{C}{\mu}RT, \qquad (1)$$

where p, i, C, μ, R, T are pressure, van't Hoff factor, concentration of solute, mollar mass, thermodynamic gas constant and temperature, and concentration is defined by formula

$C = m/V$, where m is mass of solute in volume V. If solute is sugar, $C_{12}H_{22}O_{11}$, then molar mass μ for sugar is $\mu(sugar) = 342$, because $\mu_H = 1, \mu_C = 12, \mu_O = 11$. Solvent is water H_2O, and semi-permeable membrane is thin carrot slice. In case, we consider experiment where solvent is hydrogen - H, solute is Argon - Ar, then the semi-permeable membrane is used to be the striped platinum (Pt) tube.

Svante Arrhenius later explained the physical meaning of the van't Hoff factor as the electrolytic factor. The van't Hoff factor is unit for the standard solutions.

The osmotic pressure is the (Dalton) partial pressure of solute in solution. Osmotic pressure depends only on the molar concentration of the solute but not on its identity.

If on the one side of membrane is solution (e.g. water + sugar) and on the other side is solvent (e.g. water), then, in the specific volume of solution will be less molecules of liquid solvent than in the pure liquid. Then, number of particles of the solvent striking on the membrane from the side of solution will be smaller than from the side of solvent. As result of such process the current of liquid particle to the side of solution will be greater than from the side of solution. The statistical equilibrium is broken. In order to establish equilibrium it is necessary to introduce some pressure from the side of solution. This pressure is equal to so called osmotic pressure.

The derivation of the van't Hoff formula using the thermodynamic potential can be found in the texbooks on thermodynamics and statistical physics (Landau et al., 1980). The derivation of the osmotical pressure from rigorous statistical physics was given by Isihara (1971). On the other hand, the quantum theory of osmosis was not published. A Duth physical and organic chemist van't Hoff presented his Nobelian theory long time before the introduction of photons into physics by Max Planck, Lewis and Einstein and before the introduction of phonons into solid state physics by Einstein and Debye. So, the problem of the osmotic pressure in the blackbody with the dielectric medium arises as the problem of modern physics.

So, in quantum theory of light and quantum theory of solids, it is appropriate to consider instead of pure liquid, the photon gas as solvent diffusing through the adequate membrane and phonons in the crystal as solute. It means that we can use the photon gas of the Planck blackbody outside of the dielectric crystal with the index of refraction n. Clearly speaking, if on the left side of membrane is dielectric medium with the index of refraction n and on the right side is photon gas of the blackbody, then inside of the left side of such device there is the osmotic pressure initiated by photons as solvent and phonons as solute.

The dielectric with photons is called here by term dielectric blackbody. Inside of dielectric medium with index of refraction n, the spectral radiation formula is modified and we derive in the next text its mathematical structure. The derivation of the spectral formula is based on the original Planck spectral formula which was heuristically reproduced by Einstein (1917).

2 The Einstein blackbody model

The distribution of the blackbody photons was derived by Planck (1900) from modification of the thermodynamical entropy, and later, Einstein (1919) derived the Planck formula from the Bohr model of atom which was based on two postulates 1. every atom can exist in the discrete series of states in which electrons do not radiate even if they are moving at acceleration (the postulate of the stationary states), 2. transiting electron from the stationary state to other, emits the energy according to the law $\hbar\omega = E_m - E_n$, called the Bohr formula, where E_m is the energy of an electron in the initial state, and E_n is the energy of the final state of an electron to which the transition is made and $E_m > E_n$.

Let us remark that the Bohr theory does not involve the physical mechanism of creation of photons and the adequate model of photon. However, it follows from quantum theory of fields, that photon is excited state of vacuum and at the same time also an electron is the excited state of vacuum, which follows from the elementary experimental equation $\gamma + \gamma \rightleftharpoons e^+ + e^-$ (Berestetzkii et al., 1999). At present time we know from the most general quantum field theory that all matter and antimatter in universe are excited states of vacuum.

Einstein introduced coefficients of spontaneous and stimulated emission A_{mn}, B_{mn}, B_{nm}. In case of spontaneous emission, the excited atomic state decays without external stimulus as an analogue of the natural radioactivity decay. The energy of the emitted photon is given by the Bohr formula. In the process of the stimulated emission the atom is induced by the external stimulus to make the same transition. The external stimulus is a blackbody photon that has an energy given by the Bohr formula.

If the number of the excited atoms is equal to N_m, the emission energy per unit time conditioned by the spontaneous transition from energy level E_m to energy level E_m is

$$P_{spont.\ emiss.} = N_m A_{mn}\hbar\omega, \tag{2}$$

where A_{mn} is the coefficient of the spontaneous emission.

In case of the stimulated emission, the coefficient B_{mn} corresponds to the transition of an electron from energy level E_m to energy level E_n and coefficient B_{nm} corresponds to the transition of an electron from energy level E_n to energy level E_m. So, for the energy of the stimulated emission per unit time we have two formulas :

$$P_{stimul.\ emiss.} = \varrho_\omega N_m B_{mn}\hbar\omega \tag{3}$$

$$P_{stimul.\ absorption} = \varrho_\omega N_n B_{nm}\hbar\omega. \tag{4}$$

If the blackbody is in thermal equilibrium, then the number of transitions from E_m to E_n is the same as from E_n to E_m and we write:

$$N_m A_{mn}\hbar\omega + N_m\varrho_\omega B_{mn}\hbar\omega = N_n\varrho_\omega B_{nm}\hbar\omega, \tag{5}$$

where ϱ_ω is the density of the photon energy of the blackbody.

Then, using the Maxwell statistics

$$N_n = De^{-\frac{E_n}{kT}}, \quad N_m = De^{-\frac{E_m}{kT}}, \tag{6}$$

we get:

$$\varrho_\omega = \frac{\frac{A_{mn}}{B_{mn}}}{\frac{B_{nm}}{B_{mn}} e^{\frac{\hbar\omega}{kT}} - 1}. \tag{7}$$

The spectral distribution of the blackbody does not depend on the specific atomic composition of the blackbody and it means the formula (7) must be so called the Planck formula:

$$\varrho_\omega = \frac{\hbar\omega^3}{\pi^2 c^3} \frac{1}{e^{\frac{\hbar\omega}{kT}} - 1}. \tag{8}$$

After comparison of eq. (7) with eq. (8) we get:

$$B_{mn} = B_{nm} = \frac{\pi^2 c^3}{\hbar\omega^3} A_{mn}. \tag{9}$$

It means that the probabilities of the stimulated transitions from E_m to E_n and from E_n to E_m are proportional to the probability of the spontaneous transition A_{mn}. So, it is sufficient to determine only one of the coefficient in the description of the radiation of atoms.

The internal density energy of the blackbody gas is given by integration of the last equation over all frequencies ω, or

$$u = \int_0^\infty \varrho(\omega) d\omega = aT^4; \quad a = \frac{\pi^2 k^4}{15\hbar^3 c^3} \tag{10}$$

and the pressure of photons inside the blackbody follows from the electrodymanic situation inside blackbody as follows:

$$p = \frac{u}{3} \qquad (11).$$

Let us remark that coefficients A_{mn} of the so called spontaneous emission cannot be specified in the framework of the classical thermodynamics, or, statistical physics. They can be determined only by the methods of quantum electrodynamics as the consequences of the so called radiative corrections. So, the radiative corrections are hidden external stimulus, which explains the spontaneous emission.

3 The dielectric blackbody

We suppose here that inside of the blackbody there is the dielectric medium with the index of refraction $n(\omega)$. Then, the wave vector of photon inside the dielectric medium is given by known formula

$$q = n(\omega)\frac{\omega}{c}. \tag{12}$$

The number of light modes in the interval $q, q+dq$ inside of the dielectric in the volume V is Vq^2dq/π^2. After differentiation of formula (12) we get with $d\ln\omega = d\omega/\omega$

$$dq = \frac{1}{c}[n(\omega) + \omega\frac{dn(\omega)}{d\omega}]d\omega = \frac{n(\omega)}{c}\frac{d\ln[n(\omega)\omega]}{d\ln\omega}d\omega. \tag{13}$$

Then, it is easy to see that the number of states in the interval $\omega, \omega + d\omega$ of the electromagnetic vibrations in the volume V is

$$Vg(\omega)d\omega = \frac{V}{\pi^2}\left(\frac{n(\omega)}{c}\right)^3\frac{d\ln[n(\omega)\omega]}{d\ln\omega}d\omega. \tag{14}$$

If we multiply the last formula by the average energy of the harmonic oscillator,

$$< E_\omega >= \frac{\hbar\omega}{e^{\frac{\hbar\omega}{kT}} - 1}, \tag{15}$$

we get the Planck formula for the blackbody with dielectric medium:

$$\varrho(\omega) = \frac{n^3(\omega)\omega^2}{\pi^2c^3}\frac{d\ln[n(\omega)\omega]}{d\ln\omega}\frac{\hbar\omega}{e^{\frac{\hbar\omega}{kT}} - 1}, \tag{16}$$

where for $n = 1$, we get exactly formula (8).

4 The oscillator model of the index of refraction

This model follows from the classical theory of dispersion, which is based on the vibration equation of electron in an atom

$$\ddot{x} + \gamma\dot{x} + \omega_0^2 x = \frac{e}{m}E_0\cos\omega t, \tag{17}$$

where γ is the oscillator constant and ω_0 is the basic frequency of oscillator. The symbol ω is the frequency of the applied electric field. The index of refraction following from eq (17) is given by the formula (Garbuny, 1965)

$$n = 2\pi N\frac{e^2}{m}\frac{\omega_0^2 - \omega^2}{(\omega_0^2 - \omega^2)^2 + \gamma^2\omega^2}, \tag{18}$$

where N is number of electrons in the unit of volume.

In case of electrons with basic frequencies $\omega_1, \omega_2, \omega_3, \omega_4...\omega_n$, the last refraction index can be generalized to form more complex mathematical object. We consider here, to be pedagogical clear, only one oscillator with one basic frequency. Nevertheless it is possible consider arbitrary dielectric material with the phenomenological index of refraction.

Now the question arises, if the dielectric blackbody can be considered as the solution composed from atoms, phonons and photons where the osmotic pressure play some role. We had accepted this hypothesis as the correct one.

5 The osmosis in dielectric blackbody

Phonons were introduced in the crystal physics by Einstein in order to derive the adequate formula for he specific heat. The Einstein formula was generalized and improved by Debye who derived the formula for the average energy of phonons in a crystal in the interval of temperatures $\Theta - \delta < T < \Theta + \delta$ (δ is some parameter) as follows (Rumer et al., 1977):

$$U = N\varepsilon_0 + 3NTD\left(\frac{\Theta}{T}\right), \tag{19}$$

where $\varepsilon_0 = (9/8)\hbar\omega_{max}$, where

$$\omega_{max} = 2\pi v\left(\frac{3N}{4\pi V}\right)^{1/3} \tag{20}$$

and $D(x)$ is so called the Debye wave function of the following structure:

$$D(x) = \frac{3}{x^3}\int_0^x \frac{y^3}{e^y - 1}dy, \tag{21}$$

and the critical temperature Θ was derived by Debye in the following form:

$$\Theta = v\left(\frac{6\pi^2 N}{V}\right)^{1/3}, \tag{22}$$

with v being velocity of sound waves defined in the theory of elasticity of the crystal.

Let us compare the internal energies of the pure blackbody and dielectric blackbody and then let us compare the pressure inside of the pure blackbody and inside the dielectric blackbody.

For pure blackbody, we have $u = aT^4$ and for model with n given by eq. (18) we have

$$u = \int_0^\infty \varrho_n(\omega)d\omega = \int_0^\infty \varrho_n(\omega)\frac{n^3(\omega)\omega^2}{c^3}\frac{d\ln[n(\omega)\omega]}{d\ln\omega}\frac{\hbar\omega}{e^{\frac{\hbar\omega}{kT}} - 1}d\omega. \tag{23}$$

Because the dielectric medium is permeable for photons (and not for phonons), the outer pressure is equal to the photon gas pressure in dielectric blackbody, or $p(n) = u(n)/3 = u/3$. So,

$$\int_0^\infty \varrho_n(\omega)d\omega = u/3 = \frac{aT^4}{3}, \tag{24}$$

or,

$$\int_0^\infty \frac{n^3(\omega)\omega^2}{\pi^2c^3}\frac{d\ln[n(\omega)\omega]}{d\ln\omega}\frac{\hbar\omega}{e^{\frac{\hbar\omega}{kT_{diel}}} - 1}d\omega = \frac{aT^4}{3}, \tag{25}$$

where we introduced the dielectric temperature T_{diel}, which physically means that the temperature of dielectric blackboddy is not the same as the temperature of the bath of vacuum blackbody photons. The last equation is the integral equation for function T_{diel} and in general represents very difficult mathematical problem of the future physics of the dielectric blackbody. The experimental verification of the last equation will be also the crutial problem of photon phyics.

In the most simple case with $n = const$, we get fter some algebraic operation, that the temperature dielectric blackbody surraunded by the vacuum blackbody is given by the formula

$$T_{diel} = \frac{T}{\sqrt[4]{n^3}}. \tag{26}$$

The last formula can form the goal of the experimenters working in the blackbody radiation physics. The dielectric as the osmotic membrane plays the role of the Maxwell demonic refrigerator. The second possibility is to put $n = n(T)$ in order to get the integral equation for the dependence of the index of refraction on temperature. However, it seems that this assumption is not physically adequate.

In case of the dielectric Debye crystal, the equation of state is (Rumer et al., 1977)

$$p = \left(\frac{U_{phon}}{\Theta} - \frac{9}{4}N\right)\frac{d\Theta}{dV}, \tag{27}$$

where V and N is volume and number of oscillators in crystal. The difference $\Delta p = p(T) - p(T_{diel})$ is the osmotic pressure caused by the photon flow.

In case of the two-dimensional crystal, the internal phonon energy is (Rumer et al., 1977)

$$U_{2D-phon} = \frac{4}{3}N\Theta\left[1 + \left(\frac{T}{\Theta}\right)^3 \int_0^{\Theta/T} \frac{y^2}{e^y - 1}dy\right]. \tag{28}$$

and

$$\Theta = 2\pi v \left(\frac{N}{\pi\sigma}\right)^{1/2}, \tag{29}$$

where σ is the area of the 2D crystal (e. g. graphene, which is the carbon sheet), instead of $d\Theta/dV$ is $d\Theta/d\sigma$ and 9/4 must be replaced by the adequate constant. The osmotic temperature of the 2-dimensional and 1-dimensional dielectric crystal is an analogue of the 3-dimensional case and can be derived from the formulas by author article (Pardy, 2013).

6 Discussion

Osmosis is the physical phenomenon in the system with solute, solvent, solution and semi-permeable membrane. It plays fundamental role in biological and physiological systems, where for instance the photosynthesis in plants is not posible without water and photon osmosis and human being does not exist without liquid osmosis.

Isihara (1971) derived from the statistical physics the following formula for the osmotic pressure of the two-component statistical system:

$$p = kT\frac{\partial[\ln(\Xi/\Xi_0)]}{\partial V}, \tag{30}$$

where Ξ and Ξ_0 are the big statistical sums of solute and solvent. The explicit mathematical form of the formula is sophisticated and the derivation of the van't Hoff formula is not elementary.

We have generalized the classical osmosis to the photon osmosis with phonons and photons where the osmotical pressure is realized by phonons and photons inside the medium with index of refraction. The change of temperature caused by osmotical pressure was described by eq. (25), which was solved by us only for the most simple case of the constant index of refraction. The solution of the general case is the problem of the future osmotic and photonic physics for the arbitrary index of refraction. The dielectric surface is the osmotic semi-permeable membrane and plays the role of the Maxwell demonic refrigerator.

The role of phonon-photon osmosis in biological and physiological systems is crucial. The phonon-photon osmotic pressure plays probably substantional negative role in the formation and in the development of skin cancer.

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