Thermodynamics of photon gas: Carnot cycle

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Here we discuss the thermodynamics properties of photon gas including the Carnot cycle.

Part-1

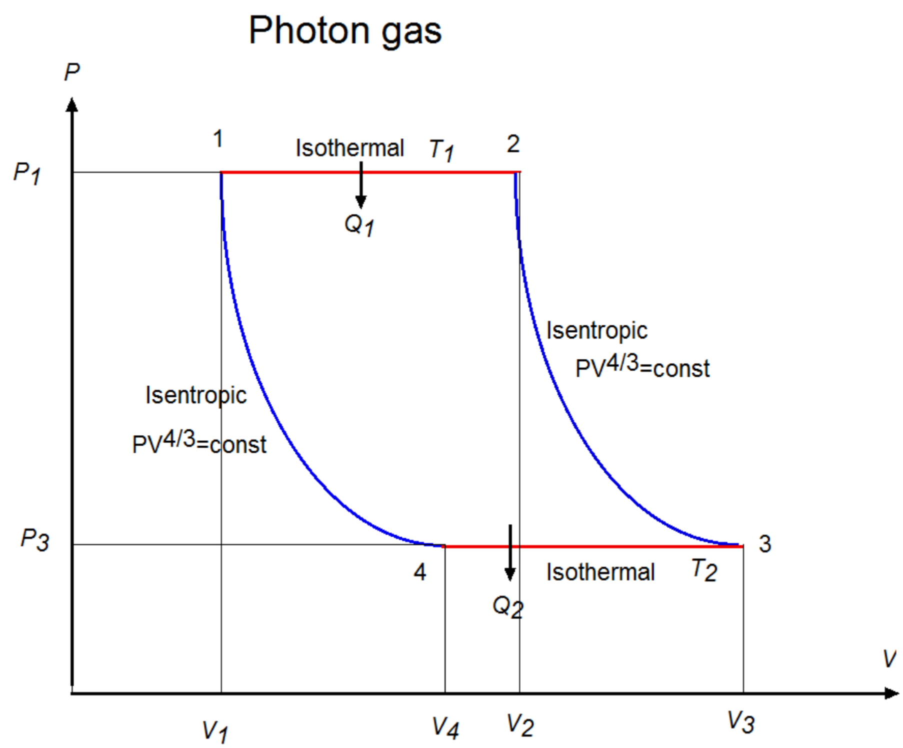
Apply the thermodynamic relation $dE = TdS - PdV$ to a photon gas. Here one can write that $E = Vu(T)$, where $u(T)$, the mean energy density of the radiation field, is independent of the volume V. The radiation pressure $P = u(T)/3$.

(a) Considering S as a function of T and V, express dS in terms of dT and dV. Find $(\partial S/\partial T)_V$ and $(\partial S/\partial V)_T$.

(b) Show that the mathematical identity $(\partial^2 S/\partial V\partial T) = (\partial^2 S/\partial T\partial V)$ gives immediately a differential equation for $u(T)$ which can be integrated to yield the Stefan Boltzmann law $u(T) \propto T^4$. In fact, it is well known that $u(T) = \frac{4\sigma_B}{c}T^4$, where the dispersion of photon is given by $\varepsilon = cp$ and the Stefan-Boltzmann constant is defined by $\sigma_B = \frac{\pi^2 k_B{}^4}{60\hbar^3 c^2}$.

Part-2 Carnot cycle

Consider a Carnot engine that uses as the working substance a photon gas (two isothermal stages 1-2 and 3-4, and two isentropic stages 2-3 and 4-1. The schematic diagram for the four processes in the P-T diagram for the photon gas is shown in Fig.



Note that the *P*-*V* diagram for the photon gas is rather different from that for the ideal gas. (c) Calculate the entropy *S* and the pressure *P* of the photon gas by using the relations given in (a) and (b).

(d) Given T_1 and T_2 ($T_1>T_2$) as well as V_1 and V_2 ($V_1>V_2$), determine V_3 and V_4.

(e) Discuss the work, the heat and the internal energy in the isothermal process (1→2). What is Q_1 transferred as heat from the high temperature reservoir at T_1 to the photon gas during this process?

(f) Discuss the work, the heat and the internal energy in the isentropic process (2→3).

(g) Discuss the work, the heat and the internal energy in the isothermal process (3→4).

(h) Discuss the work, the heat and the internal energy in the isentropic process (4→1). What is Q_2 as heat transferred from the photon gas to the low temperature reservoir at T_2 during this process ?

(i) Show the total work done by the photon gas during one cycle is given by

$$W = \frac{4\sigma_B}{3c} T_1^3 (T_1 - T_2)(V_2 - V_1)$$

(j) Show that the energy conversion efficiency for the photon gas is the Carnot efficiency for the ideal gas which is given by $\eta = \dfrac{W}{Q_1} = 1 - \dfrac{T_2}{T_1}$.

((**Solution**))

(a)

$$dU = TdS - PdV$$

where

$$U = Vu(T), \qquad P = \frac{1}{3}u(T)$$

Note that $u(T)$ is the mean energy density of the radiation field (independent of V).

$$\begin{aligned} TdS &= dU + PdV \\ &= d[Vu(T)] + \frac{1}{3}u(T)dV \\ &= \frac{4}{3}udV + V\frac{du}{dT}dT \end{aligned}$$

or

$$\begin{aligned} dS &= \frac{4}{3T}udV + \frac{V}{T}\frac{du}{dT}dT \\ &= \left(\frac{\partial S}{\partial V}\right)_T dV + \left(\frac{\partial S}{\partial T}\right)_V dT \end{aligned}$$

since S is assumed to be dependent only on V and T. Then we have

$$\left(\frac{\partial S}{\partial V}\right)_T = \frac{4u}{3T}, \qquad \left(\frac{\partial S}{\partial T}\right)_V = \frac{V}{T}\frac{du}{dT}$$

(b)

$$\frac{\partial^2 S}{\partial V \partial T} = [\frac{\partial}{\partial V}\left(\frac{\partial S}{\partial T}\right)_V]_T = \frac{1}{T}\frac{du}{dT} \qquad \text{(Maxwell's relation)}$$

$$\frac{\partial^2 S}{\partial T \partial V} = [\frac{\partial}{\partial T}\left(\frac{\partial S}{\partial V}\right)_T]_V = \frac{d}{dT}\left(\frac{4u}{3T}\right)$$

Then we have

$$\frac{1}{T}\frac{du}{dT} = \frac{d}{dT}\left(\frac{4u}{3T}\right) = \frac{4}{3}\left(\frac{T\dfrac{du}{dT} - u}{T^2}\right)$$

or

$$3T\frac{du}{dT} = 4T\frac{du}{dT} - 4u$$

or

$$3T\frac{du}{dT} = 4T\frac{du}{dT} - 4u$$

or

$$T\frac{du}{dT} = 4u$$

Then we have

$$\int \frac{1}{u} du = 4\int \frac{dT}{T}$$

$$\ln u = 4\ln T + \text{const.}$$

In conclusion, $u \propto T^4$. Note that in fact, $u(T)$ can be expressed by

$$u(T) = \frac{4\sigma_B}{c}T^4$$

(c)

$$
\begin{aligned}
TdS &= dE + PdV \\
&= d\left(\frac{4\sigma_B}{c}VT^4\right) + \frac{V\frac{4\sigma_B}{c}}{3V}T^4 dV \\
&= \frac{4\sigma_B}{c}[d(VT^4) + \frac{1}{3}T^4 dV] \\
&= \frac{4\sigma_B}{c}[4T^3 V dT + T^4 dV + \frac{1}{3}T^4 dV]
\end{aligned}
$$

Then we get

$$dS = \frac{4\sigma_B}{c}(4VT^2 dT + \frac{4}{3}T^3 dV) = \frac{4\sigma_B}{c}d\left(\frac{4}{3}VT^3\right)$$

The entropy S is given by

$$S = \frac{16\sigma_B}{3c}VT^3 + const$$

The state of equation is obtained as

$$P = \frac{E}{3V} = \frac{V\frac{4\sigma_B}{c}T^4}{3V} = \frac{4\sigma_B T^4}{3c}$$

So that the pressure P is independent of V, and depends only on T.

(d)
Process 1→2 (at $T = T_1$),: isothermal process

$$P = P_1 = \frac{4\sigma_B}{3c}T_1^4 \qquad \text{(which is independent of } V\text{)}$$

Process 3→4 (at $T = T_2$),: isothermal process

$$P = P_3 = \frac{4\sigma_B}{3c}T_2^4$$

Process 2→3, and process 4→1; isentropics process. S = const, which means that $VT^3 = const$, or $PV^{4/3} = const$ because of $P = \frac{4\sigma_B T^4}{3c}$. Here we have

$$V_2 T_1^3 = V_3 T_2^3, \qquad V_4 T_2^3 = V_1 T_1^3$$

(e)

<u>Process 1→2</u>

$$\begin{aligned}\Delta Q_{12} &= dU_{12} + PdV \\ &= \frac{4\sigma_B}{c} T_1^4 (V_2 - V_1) + \frac{4\sigma_B}{3c} T_1^4 (V_2 - V_1) \\ &= \frac{16\sigma_B}{3c} T_1^4 (V_2 - V_1)\end{aligned}$$

The heat Q_1 taken up is

$$Q_1 = \Delta Q_{12} = \frac{16\sigma_B}{3c} T_1^4 (V_2 - V_1)$$

The work done by the photon gas is

$$-\Delta W_{12} = PdV = \frac{4\sigma_B}{3c} T_1^4 (V_2 - V_1)$$

(f) Process 2→3

$$\Delta Q_{23} = 0$$

$$\begin{aligned}\Delta U_{23} &= \Delta Q_{23} + \Delta W_{23} \\ &= \Delta W_{23} \\ &= \frac{4\sigma_B}{c} V_3 T_2^4 - \frac{4\sigma_B}{c} V_2 T_1^4 \\ &= \frac{4\sigma_B}{c} [\frac{T_1^3}{T_2^3} V_2 T_2^4 - \frac{4\sigma_B}{c} V_2 T_1^4] \\ &= \frac{4\sigma_B}{c} V_2 T_1^3 (T_2 - T_1)\end{aligned}$$

(g) Process 3→4

$$\begin{aligned}\Delta Q_{34} &= dU_{34} + PdV \\ &= \frac{4\sigma_B}{c} T_2^{\,4}(V_4 - V_3) + \frac{4\sigma_B}{3c} T_2^{\,4}(V_4 - V_3) \\ &= \frac{16\sigma_B}{3c} T_2^{\,4}(V_4 - V_3) \\ &= \frac{16\sigma_B}{3c} T_1^3 T_2 (V_2 - V_1)\end{aligned}$$

The heat Q_2 is

$$Q_2 = -\Delta Q_{34} = \frac{16\sigma_B}{3c} T_1^{\,3} T_2 (V_2 - V_1)$$

The work done by the photon gas is

$$\begin{aligned}-\Delta W_{34} &= PdV \\ &= \frac{4\sigma_B}{3c} T_2^{\,4}(V_4 - V_3) \\ &= \frac{4\sigma_B}{3c} T_2 T_1^{\,3}(V_1 - V_2)\end{aligned}$$

(h) Process 4→1

$$\Delta Q_{23} = 0$$

$$\begin{aligned}\Delta U_{41} &= \Delta Q_{41} + \Delta W_{41} \\ &= \Delta W_{41} \\ &= \frac{4\sigma_B}{c}(V_1 T_1^4 - V_4 T_2^{\,4}) \\ &= \frac{4\sigma_B}{c}\left(V_1 T_1^4 - \frac{T_1^3}{T_2^{\,3}} V_1 T_2^{\,4}\right) \\ &= \frac{4\sigma_B}{c} V_1 T_1^3 (T_1 - T_2)\end{aligned}$$

(i)

The total work done by the photon gas is

$$
\begin{aligned}
-\Delta W &= W \\
&= -(\Delta W_{12} + \Delta W_{23} + \Delta W_{34} + \Delta W_{41}) \\
&= \frac{4\sigma_B}{3c}[T_1^{\,4}(V_2 - V_1) - 3V_2 T_1^{\,3}(T_2 - T_1) + T_1^{\,3} T_2 (V_1 - V_2) - 3V_1 T_1^{\,3}(T_1 - T_2)] \\
&= \frac{4\sigma_B}{3c} T_1^{\,3}(T_1 - T_2)(V_2 - V_1)
\end{aligned}
$$

(j)

$$\frac{Q_1}{T_1} = \frac{16\sigma_B}{3c} T_1^{\,3}(V_2 - V_1)$$

$$\frac{Q_2}{T_2} = \frac{16\sigma_B}{3c} T_1^{\,3}(V_2 - V_1)$$

Then we have the relation

$$\frac{Q_1}{T_1} = \frac{Q_2}{T_2}$$

$$Q_1 - Q_2 = \frac{4\sigma_B}{3c} T_1^{\,3}(T_1 - T_2)(V_2 - V_1) = W$$

The efficiency η;

$$\eta = \frac{W}{Q_1} = \frac{Q_1 - Q_2}{Q_1} = 1 - \frac{T_2}{T_1},$$

which is equal to the Carnot efficiency.

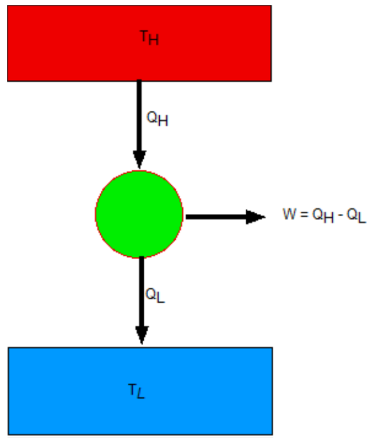


Fig. Carnot cycle. $T_H = T_1$. $T_L = T_2$. $Q_H = Q_1$. $Q_L = Q_2$. $W = Q_1 - Q_2$.

APPENDIX

2. (Point 40)

Photon gas: (a) Ignoring the zero-point energy, show that the partition function Z for a gas of photons in volume V is given by

$$\ln Z = -\frac{V}{\pi^2 c^3}\int_0^\infty \omega^2 \ln(1-e^{-\beta\hbar\omega})d\omega,$$

and hence, by integrating by parts, that

$$\ln Z = \frac{V\pi^2 (k_B T)^3}{45\hbar^3 c^3}$$

$$\int_0^\infty \frac{x^3}{\exp(x)-1}dx = \frac{\pi^4}{15}.$$

(b) Show that

$$F = -\frac{4\sigma_{SB} V T^4}{3c},\quad S = \frac{16\sigma_{SB} V T^3}{3c},\quad U = \frac{4\sigma_{SB} V T^4}{c},\quad P = \frac{4\sigma_{SB} T^4}{3c},$$

and hence that

$$U = -3F,\quad PV = \frac{U}{3},\ \text{and}\ S = \frac{4U}{3T},$$

where $\sigma_{SB} = \dfrac{\pi^2 k_B{}^4}{60\hbar^3 c^2}$ is the Stefan-Boltzmann constant.

((Solution))

Helmholtz free energy F;

Using the one particle partition function for the mode with $|\boldsymbol{k}\rangle$

$$Z_{1k} = \sum_{n=0}^{\infty} \exp(-n\beta\hbar\omega_k) = \frac{1}{1-\exp(-\beta\hbar\omega_k)}$$

we have the partition function for the total system (canonical ensemble)

$$Z_C = \prod_{\boldsymbol{k}} Z_{1\boldsymbol{k}}$$

or

$$\begin{aligned}
\ln Z_C &= -\sum_{\boldsymbol{k}} \ln(1-e^{-\beta\hbar\omega_{\boldsymbol{k}}}) \\
&= -\frac{2V}{(2\pi)^3}\int 4\pi k^2 dk \ln(1-e^{-\beta\hbar\omega_{\boldsymbol{k}}}) \\
&= -\frac{2V}{(2\pi)^3} 4\pi \int \frac{\omega^2}{c^3} d\omega \ln(1-e^{-\beta\hbar\omega}) \\
&= -\frac{V}{\pi^2 c^3}\int \omega^2 d\omega \ln(1-e^{-\beta\hbar\omega})
\end{aligned}$$

where the factor 2 comes from the two kinds of the polarization vectors, and $\omega_{\boldsymbol{k}} = ck$. Taking the integral,

$$\begin{aligned}
\ln Z_C &= \frac{2V}{(2\pi)^3}\frac{4\pi}{3c^3}\beta\hbar\int_0^{\infty}\omega^3 \frac{1}{e^{\beta\hbar\omega}-1} d\omega \\
&= \frac{2V}{(2\pi)^3}\frac{4\pi}{3c^3}\frac{1}{(\beta\hbar)^3}\int_0^{\infty}\frac{x^3}{e^x-1}dx \\
&= \frac{V}{3\pi^2 c^3}\frac{1}{(\beta\hbar)^3}\int_0^{\infty}\frac{x^3}{e^x-1}dx
\end{aligned}$$

$$\begin{aligned}
F &= -k_B T \ln Z_C \\
&= -k_B T \frac{V}{3\pi^2 c^3}\frac{1}{(\beta\hbar)^3}\int_0^{\infty}\frac{x^3}{e^x-1}dx
\end{aligned}$$

The integration by part leads to

$$\frac{F}{V} = -\frac{{k_B}^4}{3\pi^2\hbar^3 c^3}T^4\int_0^{\infty}\frac{x^3 dx}{e^x-1} = -\frac{1}{45}\frac{\pi^2 {k_B}^4}{\hbar^3 c^3}T^4 = -\frac{4}{3c}\sigma_{SB}T^4$$

or

$$F = -\frac{4\sigma_{SB}V}{3c}T^4$$

where

$$\int_0^\infty \frac{x^3 dx}{e^x - 1} = \frac{\pi^4}{15}$$

or

$$F = -\frac{1}{3}U$$

using the value of U.

We note that

$$\ln Z_C = \frac{4\sigma_{SB}V}{3ck_B}T^3$$

The entropy S:

$$S = -(\frac{\partial F}{\partial T})_V = \frac{16\sigma_{SB}V}{3c}T^3 = \frac{4U}{3T}$$

The total energy:

$$U = F + ST = -\frac{4\sigma_{SB}V}{3c}T^4 + \frac{16\sigma_{SB}V}{3c}T^4 = \frac{4\sigma_{SB}V}{c}T^4 = -3F$$

The pressure:

$$P = -(\frac{\partial F}{\partial V})_T = \frac{4\sigma_{SB}}{3c}T^4 = \frac{U}{3V}$$

The Gibbs free energy:

$$G = \mu N = F + PV = -\frac{1}{3}U + \frac{1}{3}U = 0$$

leading to

$$\mu = 0$$

In other words, the chemical potential is zero for the photon gas.

The Stefan Boltzmann constant:

$$\sigma_{SB} = \frac{c}{4}[\frac{\pi^2 k_B{}^4}{15(\hbar c)^3}] = \frac{\pi^2 k_B{}^4}{60\hbar^3 c^2} = 5.670367 \text{ x } 10^{-8} \text{ W/(m}^2\text{K}^4)$$