The Energy, and Entropy of Photons and Electrons

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June, 2020
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Abstract:

PHOTONS: We show how Planck created the probabilistic Entropy and obtained the entropy, and the energy of photon gas.

We complete Planck's work by showing the equivalence for the photon gas between Planck’s Energy Law, the entropy, and the approximated Boson statistics.

ELECTRONS: Fermi, and later Dirac, unaware of Boltzmann's work, followed Bose, with clarity which was beyond Bose.

They obtained partial results for the entropy and the energy for the electron gas. And concluded with the energy law

$$\bar{\varepsilon}_l = \frac{\varepsilon_l}{e^{\alpha}e^{\beta\varepsilon_l} + 1}$$

They did not know how to determine the α, and the β constants.

Indeed, the α results from a flaw in their analysis[1].

The β can be determined, and we give the derivation they missed.

For the electron gas, we show the equivalence between the Energy Law, the entropy, and the Fermions statistics.

We obtain an even simpler derivation of the entropy and the energy laws for the electron gas by using Planck's approach directly.

IDEAL GAS: The molecules of ideal gas have the same statistics of photons. But being particles, they don't need to be assumed particles. Thus, ideal gas have been treated by Boltzmann, without the quantum hypothesis.

Boltzmann was later plagiarized by Bose and Einstein.

We apply Boltzmann results to sparse photon gas, and to sparse electron gas.

We derive ideal gas entropy from photon's entropy, and conclude with ideal gas condensation.

BOSE-EINSTEIN: Bose applied Planck's quantum law that radiation energy is discrete, and Planck's entropy law that $s = k \log W$, with no recognition of Planck, to derive the Planck's entropy for the photon-gas.

Bose followed Boltzmann, and contributed nothing new to entropy.

But his derivation allowed us to easily establish condensation of neutral molecules at low enough temperatures.

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[1] In a more general setting $\mu = \alpha k T$ is a chemical potential per particle

Keywords: Probabilistic Entropy, Maximal Entropy, Electromagnetic Radiation, Photon Gas, Heat Radiation, Blackbody Radiation, Planck's Radiation Law, Quantized Radiation, Radiation Quantum, Entropy Constant k, Quantum Constant h, Bose-Einstein, Condensation,

PACS 12.90.+b.

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0.

Boltzmann's Entropy

Boltzmann pioneered the probabilistic view of entropy, and attempted to derive the entropy of ideal gas from the statistical point of view.

But without Planck's quantum hypothesis that radiation energy is discrete, and without Planck's Radiation Law, this task was beyond Boltzmann.

In fact, the Boltzmann equation

$$s = -k \log W$$

was derived by Planck.

And the Boltzmann constant

$$k$$

that appears in the equation was defined and determined by Planck.

Since 1877, there was no derivation of Boltzmann's probabilistic entropy, that avoided Planck's quantum hypothesis, and Planck's radiation law.

In particular, Bose derivation of entropy is plagiarizing of Boltzmann's derivation that assumes Planck's quantum hypothesis, and Planck's

$$s = -k \log W .$$

I. PHOTONS

1.

Planck's Probabilistic Entropy

Planck attempted to derive the probability distribution for the quantized energy, and quantized entropy by applying Boltzmann Probabilistic approach to Entropy.

We assume

$$N \quad \text{Molecules}$$

distributed in a

$$\text{Volume } V.$$

$$N_1 \text{ in volume } \delta V_1\text{, with probability } p_1 = \frac{N_1}{N}$$

$$N_2 \text{ in volume } \delta V_2\text{, with probability } p_2 = \frac{N_2}{N}$$

$$N_3 \text{ in volume } \delta V_3\text{, with probability } p_3 = \frac{N_3}{N}$$

....

$$N = N_1 + N_2 + N_3 + ...,$$

$$1 = p_1 + p_2 + p_3 + ...$$

The state of the molecule system

$$A(N_1, N_2, N_3, ...)$$

is determined by the numbers

$$N_1,\ N_2,\ N_3, ...$$

or, alternatively, by the probabilities

$$p_1,\ p_2,\ p_3, \ldots\ldots\ldots\ldots$$

The state A has

$$\boxed{W(A) = W(N_1, N_2, N_3, \ldots) = \frac{N!}{N_1!N_2!N_3!\ldots..}}$$

such combinations.

The probability of each combination is

$$p(A) = p(N_1, N_2, N_3, \ldots) = \frac{1}{W(N_1, N_2, N_3, \ldots)} = \frac{N_1!N_2!N_3!\ldots..}{N!}.$$

We define the entropy of the state,

$$S(A) = S(W) = S(N_1, N_2, N_3, \ldots),$$

to depend only on the number of the combinations so that

For independent states A_1, and A_2

$$\textbf{(I)} \qquad p(A_1 \wedge A_2) = p(A_1)p(A_2)$$

$$\textbf{(II)} \quad S(W_1) + S(W_2) = S(\underbrace{W_1W_2}_{W}).$$

Then we have

1.1 $$\boxed{S(W) = k\log W + \text{const}},$$

$$k = \text{the } \textbf{Entropy Constant}^2$$

Proof:

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[2] While **Planck** articulates that the **Entropy Constant** k is his, he attributes his own entropy equation $S = k\log W$ to Boltzmann, Thus, k became known as **Boltzmann Constant**. But it was **defined and determined** by **Planck**. Planck's ingenuity shows in his treatment of the entropy, and in his determination of k, and h. See The Entropy Constant k, The Radiation Constant h, The Quantized 2nd Law, The Quantized Temperature, & The Temperature Quantum", Gauge Institute Journal of Math and Physics, Vol.15 No 1, February 2019.

$\partial_{W_1}(II) \Rightarrow$

$$\partial_{W_1} S(W_1) + \underbrace{\partial_{W_1} S(W_2)}_{0} = \partial_{W_1} S(W_1 W_2)$$

$$= \underbrace{\partial_W S(W)}_{S'(W)} \underbrace{\partial_{W_1}\{W_1 W_2)}_{W_2}$$

$$\Rightarrow \qquad \partial_{W_1} S(W_1) = S'(W) W_2$$

$$\underbrace{\partial_{W_2}\{\partial_{W_1} S(W_1)\}}_{0} = \partial_{W_2}\{S'(W) W_2\}$$

$$= \underbrace{\partial_W S'(W)}_{S''(W)} \underbrace{\partial_{W_2}(W)}_{W_1} W_2 + S'(W)$$

$$= S''(W) \underbrace{W_1 W_2}_{W} + S'(W)$$

$$0 = \underbrace{WS''(W) + S'(W)}_{\left(WS'(W)\right)'}.$$

$$\big(WS'(W)\big)' = 0$$

$$WS'(W) = k = \text{ the entropy constant}$$

$$S'(W) = \frac{k}{W}$$

$$S(W) = k \int \frac{1}{W} dW + \text{const}$$

$$S(W) = k \log W + \text{const}. \square$$

1.2 $\boxed{\log W = -N(p_1 \log p_1 + p_2 \log p_2 + ...)}$

Proof: By Sterling's approximation, for large n, $n! \sim n^n e^{-n} \sqrt{2\pi n}$

Therefore,

$$N_1! \sim N_1^{N_1} e^{-N_1} \sqrt{2\pi N_1}\,,$$

$$N_2! \sim N_2^{N_2} e^{-N_2} \sqrt{2\pi N_2}\,,$$

$$\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots$$

$$W = \frac{N!}{N_1!N_2!N_3!\dots\dots}$$

$$= \frac{N^N e^{-N}\sqrt{2\pi N}}{N_1^{N_1}e^{-N_1}\sqrt{2\pi N_1}N_2^{N_2}e^{-N_2}\sqrt{2\pi N_2}N_3^{N_3}e^{-N_3}\sqrt{2\pi N_3}\dots\dots\dots}$$

$$= \frac{N^N\sqrt{2\pi N}}{N_1^{N_1}\sqrt{2\pi N_1}N_2^{N_2}\sqrt{2\pi N_2}N_3^{N_3}\sqrt{2\pi N_3}\dots\dots\dots}$$

$$\log W = (N\log N + \tfrac{1}{2}\log 2\pi N) - (N_1\log N_1 + \tfrac{1}{2}\log 2\pi N_1)$$

$$-(N_2\log N_2 + \tfrac{1}{2}\log 2\pi N_2) - \dots.$$

$$\approx N\log N - \underbrace{N_1}_{p_1N}\log N_1 - \underbrace{N_2}_{p_2N}\log N_2 - \dots.$$

$$= N\log N - Np_1(\log p_1 + \log N) - Np_2(\log p_2 + \log N) - \dots.$$

$$= N\log N\underbrace{(1 - p_1 - p_2 - \dots)}_{0} - N(p_1\log p_1 + p_2\log p_2 + \dots)$$

$$= -N(p_1\log p_1 + p_2\log p_2 + \dots).\square$$

2.

The Energy and Entropy of Photon-Gas, Planck's Way

2.1 The Average Entropy per unit volume, at frequency ν is

$$\boxed{\overline{s_\nu} = k\left\{\left(\frac{\overline{\varepsilon_\nu}}{h\nu}+1\right)\log\left(\frac{\overline{\varepsilon_\nu}}{h\nu}+1\right)-\left(\frac{\overline{\varepsilon_\nu}}{h\nu}\right)\log\left(\frac{\overline{\varepsilon_\nu}}{h\nu}\right)\right\}}$$

Proof: Following Planck's 1912 oscillator model, we assume a probability

$$p_\nu$$

for the oscillator to radiate,

and a probability

$$q_\nu = 1 - p_\nu$$

to not radiate.

We assume radiation of

$$h\nu \text{ with probability } p_{\nu,1},$$

$$2h\nu \text{ with probability } p_{\nu,2} = p_{\nu,1}q_\nu,$$

$$3h\nu \text{ with probability } p_{\nu,n} = p_{\nu,1}q_\nu^2,$$

……………………………………………….

Since

$$1 = p_{\nu,1} + p_{\nu,2} + ...,$$

$$= p_{\nu,1}(1 + q_\nu + q_\nu^2 + ...)$$

$$= \frac{p_{\nu,1}}{1-q_\nu}$$

$$= \frac{p_{\nu,1}}{p_\nu}.$$

we have

$$p_{\nu,1} = p_\nu, \quad \text{and} \quad p_{\nu,n} = p_\nu q_\nu^{n-1}.$$

Therefore, the oscillator's average entropy at frequency ν is

$$\overline{s_\nu} = -k\Big(p_\nu \log p_\nu + p_\nu q_\nu \log p_\nu q_\nu + p_\nu q_\nu^2 \log p_\nu q_\nu^2 + ...\Big)$$

$$= -kp_\nu \Big(\log p_\nu + q_\nu \log p_\nu q_\nu + q_\nu^2 \log p_\nu q_\nu^2 + ...\Big)$$

$$= -kp_\nu \log p_\nu \Big(1 + q_\nu + q_\nu^2 + ...\Big) - (kp_\nu q_\nu \ln q_\nu)\Big(1 + 2q_\nu + 3q_\nu^2 + ...\Big)$$

$$= -(kp_\nu \log p_\nu)\frac{1}{1-q_\nu} - (kp_\nu q_\nu \ln q_\nu)\frac{d}{dq_\nu}\Big(1 + q_\nu + q_\nu^2 + ...\Big)$$

$$= -(kp_\nu \log p_\nu)\frac{1}{1-q_\nu} - (kp_\nu q_\nu \log q_\nu)\frac{d}{dq_\nu}\frac{1}{1-q_\nu}$$

$$= -(kp_\nu \log p_\nu)\frac{1}{1-q_\nu} - (kp_\nu q_\nu \log q_\nu)\frac{1}{(1-q_\nu)^2}$$

$$= -k \log p_\nu - k\frac{1-p_\nu}{p_\nu}\ln(1-p_\nu)$$

$$= k\left\{ -\log p_\nu - \frac{1-p_\nu}{p_\nu}\log\frac{1-p_\nu}{p_\nu} - \frac{1-p_\nu}{p_\nu}\log p_\nu \right\}$$

$$= k\left\{ \frac{1}{p_\nu}\log\frac{1}{p_\nu} - (\frac{1}{p_\nu} - 1)\log(\frac{1}{p_\nu} - 1) \right\}.$$

The average radiation energy of an oscillator is

$$\overline{\varepsilon_\nu} = h\nu p_\nu + 2h\nu p_\nu q_\nu + 3h\nu p_\nu q_\nu^2 + 4h\nu p_\nu q_\nu^3 + ...$$

$$= h\nu p_\nu \left\{1 + 2q_\nu + 3q_\nu^2 + 4q_\nu^3 + ...\right\}$$

$$= h\nu p_\nu \left\{\left(1 + q_\nu + q_\nu^2 + q_\nu^3 ...\right) + q_\nu \left(1 + 2q_\nu + 3q_\nu^2 ...\right)\right\}$$

$$= h\nu p_\nu \left\{\frac{1}{1-q_\nu} + q_\nu \frac{d}{dq_\nu}\left(1 + q_\nu + q_\nu^2 + q_\nu^3 ...\right)\right\}$$

$$= h\nu p_\nu \left\{\frac{1}{p_\nu} + q_\nu \frac{d}{dq_\nu}\frac{1}{1-q_\nu}\right\}$$

$$= h\nu p_\nu \left\{\frac{1}{p_\nu} + q_\nu \frac{1}{(1-q_\nu)^2}\right\}$$

$$= h\nu \left\{\frac{p_\nu}{p_\nu} + p_\nu q_\nu \frac{1}{p_\nu^2}\right\}$$

$$= h\nu \frac{p_\nu + q_\nu}{p_\nu}$$

$$= h\nu \frac{1}{p_\nu}$$

Thus,

$$\frac{1}{p_\nu} = \frac{\overline{\varepsilon_\nu}}{h\nu}$$

Therefore

$$\overline{s_\nu} = k\left\{\left(\frac{\overline{\varepsilon_\nu}}{h\nu} + 1\right)\log\left(\frac{\overline{\varepsilon_\nu}}{h\nu} + 1\right) - \left(\frac{\overline{\varepsilon_\nu}}{h\nu}\right)\log\left(\frac{\overline{\varepsilon_\nu}}{h\nu}\right)\right\}.\square$$

2.2 Planck Radiation Law:

The Average Radiation Energy per unit volume, at Frequency ν is

$$\overline{\varepsilon_\nu} = \frac{h\nu}{e^{\frac{h\nu}{kT}} - 1}$$

Proof:

$$\underbrace{\frac{\partial \overline{s_\nu}}{\partial \overline{\varepsilon_\nu}}}_{\frac{1}{T}} = k\left\{\frac{1}{h\nu}\log\left(\frac{\overline{\varepsilon_\nu}}{h\nu} + 1\right) - \frac{1}{h\nu}\log\frac{\overline{\varepsilon_\nu}}{h\nu}\right\},$$

$$= k\frac{1}{h\nu}\log\frac{\frac{\overline{\varepsilon_\nu}}{h\nu} + 1}{\frac{\overline{\varepsilon_\nu}}{h\nu}},$$

$$= k\frac{1}{h\nu}\log\left(1 + \frac{h\nu}{\overline{\varepsilon_\nu}}\right).$$

Hence,

$$\frac{1}{T} = k\frac{1}{h\nu}\log\left(1 + \frac{h\nu}{\overline{\varepsilon_\nu}}\right),$$

$$e^{\frac{h\nu}{kT}} = 1 + \frac{h\nu}{\overline{\varepsilon_\nu}},$$

$$e^{\frac{h\nu}{kT}} - 1 = \frac{h\nu}{\overline{\varepsilon_\nu}},$$

$$\overline{\varepsilon_\nu} = \frac{h\nu}{e^{\frac{h\nu}{kT}} - 1}.\square$$

3.

The Entropy, and Energy of Photon-Gas, the Easy Way

We assume that

$$\text{Energy is radiated in multiples of } h\nu,$$

And that the entropy is

$$S(W) = k\log W,$$

And that at frequency ν.

$$N_\nu \text{ photons } h\nu \text{ are distributed between } Z_\nu \text{ radiators}$$

Thus,

$$N_\nu h\nu = Z_\nu \overline{\varepsilon}_\nu .$$

Then

3.1 The following are equivalent

♦The average radiation energy per unit volume at frequency ν is

$$\overline{\varepsilon}_\nu = \frac{h\nu}{e^{\frac{h\nu}{kT}} - 1}.$$

♦The average entropy per unit volume at frequency ν is

$$\overline{s}_\nu = k\left\{\left(\frac{\overline{\varepsilon}_\nu}{h\nu} + 1\right)\log\left(\frac{\overline{\varepsilon}_\nu}{h\nu} + 1\right) - \frac{\overline{\varepsilon}_\nu}{h\nu}\log\frac{\overline{\varepsilon}_\nu}{h\nu}\right\}$$

◆ $$W_{Z_\nu} \approx \frac{\left(N_\nu + Z_\nu - 1\right)!}{N_\nu!\left(Z_\nu - 1\right)!}$$

<u>Proof</u>:

$(\overline{\varepsilon}_\nu \Leftrightarrow \overline{s}_\nu)$

$$\overline{\varepsilon}_\nu = \frac{h\nu}{e^{\frac{h\nu}{kT}} - 1},$$

$$e^{\frac{h\nu}{kT}} - 1 = \frac{h\nu}{\overline{\varepsilon}_\nu},$$

$$e^{\frac{h\nu}{kT}} = \frac{h\nu}{\overline{\varepsilon}_\nu} + 1,$$

$$\frac{h\nu}{kT} = \log\left(\frac{h\nu}{\overline{\varepsilon}_\nu} + 1\right),$$

$$\underbrace{\frac{1}{T}}_{\frac{\partial \overline{s}_\nu}{\partial \overline{\varepsilon}_\nu}} = \frac{k}{h\nu}\log\left(\frac{h\nu}{\overline{\varepsilon}_\nu} + 1\right),$$

$$\frac{\partial \overline{s}_\nu}{\partial \overline{\varepsilon}_\nu} = \frac{k}{h\nu}\log\left(\frac{h\nu}{\overline{\varepsilon}_\nu} + 1\right),$$

$$= k\frac{1}{h\nu}\log\frac{1 + \frac{\overline{\varepsilon}_\nu}{h\nu}}{\frac{\overline{\varepsilon}_\nu}{h\nu}},$$

$$= k\left\{\frac{1}{h\nu}\log\left(1 + \frac{\overline{\varepsilon}_\nu}{h\nu}\right) - \frac{1}{h\nu}\log\frac{\overline{\varepsilon}_\nu}{h\nu}\right\}$$

$$\overline{s_{\nu}} = k\left\{\left(1+\frac{\overline{\varepsilon}_{\nu}}{h\nu}\right)\log\left(1+\frac{\overline{\varepsilon}_{\nu}}{h\nu}\right)-\frac{\overline{\varepsilon}_{\nu}}{h\nu}\log\frac{\overline{\varepsilon}_{\nu}}{h\nu}\right\}.\square$$

$(\overline{s}_{\nu} \Leftrightarrow W_{Z_{\nu}})$

Since $\frac{\overline{\varepsilon}_{\nu}}{h\nu} = \frac{N_{\nu}}{Z_{\nu}}$,

$$\overline{s}_{\nu} = k\left\{\left(\frac{N_{\nu}}{Z_{\nu}}+1\right)\log\left(\frac{N_{\nu}}{Z_{\nu}}+1\right)-\frac{N_{\nu}}{Z_{\nu}}\log\frac{N_{\nu}}{Z_{\nu}}\right\}.$$

So the entropy of the N_{ν} photons per unit volume at ν is

$$S_{Z_{\nu}} = Z_{\nu}\overline{s}_{\nu}$$

$$= k\left\{(N_{\nu}+Z_{\nu})\left(\log(N_{\nu}+Z_{\nu})-\log Z_{\nu}\right)-N_{\nu}\left(\log N_{\nu}-\log Z_{\nu}\right)\right\}$$

Using Sterling's formula $\log M! \approx M\log M - M$,

$$S_{Z_{\nu}} \approx k\left\{\log\left(N_{\nu}+Z_{\nu}\right)! + N_{\nu}+Z_{\nu}-\ln Z_{\nu}! - Z_{\nu}-\ln N_{\nu}! - N_{\nu}\right\}$$

$$= k\left\{\log\left(N_{\nu}+Z_{\nu}\right)! - \ln Z_{\nu}! - \ln N_{\nu}!\right\}$$

$$= k\log\frac{\left(N_{\nu}+Z_{\nu}\right)!}{N_{\nu}!Z_{\nu}!}.$$

That is, the N_{ν} photons can be distributed among the Z_{ν} radiators in

$$W_{Z_{\nu}} \approx \frac{\left(N_{\nu}+Z_{\nu}\right)!}{N_{\nu}!Z_{\nu}!} \approx \frac{\left(N_{\nu}+Z_{\nu}-1\right)!}{N_{\nu}!(Z_{\nu}-1)!}$$

ways.□

II. ELECTRONS

4.

The Energy and Entropy of Electron-Gas, Boltzmann Way

Fermi, and later Dirac obtained partial results for the entropy and the energy of electron gas.

Fermi and Dirac concluded with the energy law

$$\overline{\varepsilon}_l = \frac{\varepsilon_l}{e^{\alpha}e^{\beta\varepsilon_l} + 1}$$

They did not know how to determine the α, and the β constants.

Indeed, the α results from a flaw in their analysis.

The β can be determined.

In the following, we give the derivation they missed.

We assume that

Energy of electrons ε_l is multiple of discrete energy unit,

And that the entropy is

$$S(W) = k \log W\,,$$

And that

N_1 electrons at energy ε_1 are distributed between Z_1 cells

N_2 electrons at energy ε_2 are distributed between Z_2 cells

N_3 electrons at energy ε_3 are distributed between Z_3 cells

……………………………………………………………………………………

The cells have one electron, or no electrons

That is, there are more cells than electrons

$$Z_l \geq N_l,$$

and

$$N_l \varepsilon_l = Z_l \overline{\varepsilon}_l,$$

For each $l = 1, 2, 3, \ldots$,

the N_l electrons can be arranged in

$$\frac{Z_l!}{N_l!(Z_l - N_l)!}$$

ways.

Thus, all the electrons can be arranged in

$$w = \frac{Z_1!}{N_1!(Z_1 - N_1)!} \times \frac{Z_2!}{N_2!(Z_2 - N_2)!} \times \frac{Z_3!}{N_3!(Z_3 - N_3)!} \times \ldots$$

ways.

The entropy per volume element is

$$s = k \log w = k \sum_{l=1}^{l=l_{\max}} \log(Z_l!) - k \sum_{l=1}^{l=l_{\max}} \log(N_l!) - k \sum_{l=1}^{l=l_{\max}} \log([Z_l - N_l]!),$$

where k is the Entropy Constant.

By Sterling's formula $\log M! \approx M(\log M - 1)$,

$$s \approx k \sum_{l=1}^{l=l_{\max}} Z_l(\log Z_l - 1) - k \sum_{l=1}^{l=l_{\max}} N_l(\log N_l - 1)$$

$$-k \sum_{l=1}^{l=l_{\max}} [Z_l - N_l](\log[Z_l - N_l] - 1)$$

$$= k \sum_{l=1}^{l=l_{\max}} Z_l \log Z_l - k \sum_{l=1}^{l=l_{\max}} N_l \log N_l - k \sum_{l=1}^{l=l_{\max}} [Z_l - N_l] \log[Z_l - N_l]$$

The energy per unit volume is

$$u = N_1\varepsilon_1 + N_2\varepsilon_2 + N_3\varepsilon_3 + \ldots.$$

At thermal equilibrium, the entropy has a maximum under this constraint.

We apply the Lagrange multiplier method with multiplier

$$\beta > 0,$$

to the auxiliary function

$$\Phi(N_l, \beta) = k \sum_{l=1}^{l=l_{\max}} Z_l \log Z_l - k \sum_{l=1}^{l=l_{\max}} N_l \log N_l - k \sum_{l=1}^{l=l_{\max}} [Z_l - N_l] \log[Z_l - N_l]$$

$$+\beta(u - \sum_{l=1}^{l=l_{\max}} N_l \varepsilon_l).$$

The critical points are at

$$0 = \frac{\partial \Phi}{\partial N_l} = -\underbrace{\frac{\partial}{\partial N_l}\left(N_l \log N_l\right)}_{\log N_l + N_l \frac{1}{N_l}} - \underbrace{\frac{\partial}{\partial N_l}[Z_l - N_l]\log[Z_l - N_l]}_{-\log[Z_l - N_l] + [Z_l - N_l]\frac{1}{[Z_l - N_l]}(-1)} - \beta\varepsilon_l,$$

$$= -\log N_l + \log[Z_l - N_l] - \beta\varepsilon_l.$$

$$\Rightarrow \qquad \log\left(\frac{Z_l}{N_l} - 1\right) = \beta\varepsilon_l$$

$$\frac{Z_l}{N_l} - 1 = e^{\beta\varepsilon_l}$$

$$\underbrace{\frac{Z_l}{N_l}}_{\frac{\varepsilon_l}{\overline{\varepsilon}_l}} = e^{\beta\varepsilon_l} + 1$$

$$\overline{\varepsilon}_l = \frac{\varepsilon_l}{e^{\beta\varepsilon_l} + 1}.$$

To determine β, we need the entropy per unit volume

$$S_l = Z_l \overline{s}_l.$$

We recall that N_l electrons per unit volume, per mode l can be distributed among the Z_l cells in

$$W_l \approx \frac{Z_l!}{N_l!\left(Z_l - N_l\right)!}$$

ways.

$$S_l = k\log\frac{Z_l!}{N_l!\left(Z_l - N_l\right)!}$$

$$= k\left\{-\log(Z_l - N_l)! + \log Z_l! - \log N_l!\right\}$$

$$= k\left\{-\log(Z_l - N_l)! - (Z_l - N_l) + \log Z_l! + Z_l - \log N_l! - N_l\right\}$$

Using Sterling's formula $\log M! \approx M\log M - M$,

$$S_l = k\left\{-(Z_l - N_l)\log(Z_l - N_l) + Z_l\log Z_l - N_l\log N_l\right\}$$

$$= k\left\{-(Z_l - N_l)\log(Z_l - N_l)\underbrace{-N_l\log Z_l} + Z_l\log Z_l - N_l\log N_l\underbrace{+N_l\log Z_l}\right\}$$

$$= k\left\{(N_l - Z_l)\left(\log(Z_l - N_l) - \log Z_l\right) - N_l\left(\log N_l - \log Z_l\right)\right\}$$

$$= k\left\{(N_l - Z_l)\log\frac{Z_l - N_l}{Z_l} - N_l\log\frac{N_l}{Z_l}\right\}$$

$$= k\left\{(N_l - Z_l)\log\left(1 - \frac{N_l}{Z_l}\right) - N_l\log\frac{N_l}{Z_l}\right\}$$

$$\underbrace{\frac{S_l}{Z_l}}_{\overline{s}_l} = k\left\{\left(\frac{N_l}{Z_l} - 1\right)\log\left(1 - \frac{N_l}{Z_l}\right) - \frac{N_l}{Z_l}\log\frac{N_l}{Z_l}\right\}$$

Since $\frac{N_l}{Z_l} = \frac{\overline{\varepsilon}_l}{\varepsilon_l}$, the average entropy of the electron gas is

$$\boxed{\overline{s}_l = k\left\{\left(\frac{\overline{\varepsilon}_l}{\varepsilon_l} - 1\right)\log\left(1 - \frac{\overline{\varepsilon}_l}{\varepsilon_l}\right) - \frac{\overline{\varepsilon}_l}{\varepsilon_l}\log\frac{\overline{\varepsilon}_l}{\varepsilon_l}\right\}}.$$

$$\frac{\partial\overline{s}_l}{\partial\overline{\varepsilon}_l} = k\underbrace{\frac{\partial}{\partial\overline{\varepsilon}_l}\left(\frac{\overline{\varepsilon}_l}{\varepsilon_l} - 1\right)\log\left(1 - \frac{\overline{\varepsilon}_l}{\varepsilon_l}\right)}_{\frac{1}{\varepsilon_l}\log\left(1-\frac{\overline{\varepsilon}_l}{\varepsilon_l}\right)+\left(\frac{\overline{\varepsilon}_l}{\varepsilon_l}-1\right)\frac{1}{\left(1-\frac{\overline{\varepsilon}_l}{\varepsilon_l}\right)}\left(-\frac{1}{\varepsilon_l}\right)} - k\underbrace{\frac{\partial}{\partial\overline{\varepsilon}_l}\frac{\overline{\varepsilon}_l}{\varepsilon_l}\log\frac{\overline{\varepsilon}_l}{\varepsilon_l}}_{\frac{1}{\varepsilon_l}\log\frac{\overline{\varepsilon}_l}{\varepsilon_l}+\frac{\overline{\varepsilon}_l}{\varepsilon_l}\frac{1}{\left(\frac{\overline{\varepsilon}_l}{\varepsilon_l}\right)}\left(\frac{1}{\varepsilon_l}\right)}$$

$$= k\left\{\frac{1}{\varepsilon_l}\log\left(1 - \frac{\overline{\varepsilon}_l}{\varepsilon_l}\right) - \frac{1}{\varepsilon_l}\log\frac{\overline{\varepsilon}_l}{\varepsilon_l}\right\}$$

$$= \frac{k}{\varepsilon_l}\log\frac{1 - \frac{\overline{\varepsilon}_l}{\varepsilon_l}}{\frac{\overline{\varepsilon}_l}{\varepsilon_l}}$$

$$= \frac{k}{\varepsilon_l}\underbrace{\log\left(\frac{\varepsilon_l}{\overline{\varepsilon}_l} - 1\right)}_{\beta\varepsilon_l}$$

$$= k\beta.$$

That is,

$$\underbrace{\frac{\partial \overline{s}_l}{\partial \overline{\varepsilon}_l}}_{\frac{1}{T}} = k\beta$$

$$\beta = \frac{1}{kT}$$

And the energy law for the electron gas is

$$\boxed{\overline{\varepsilon}_l = \frac{\varepsilon_l}{e^{\frac{\varepsilon_l}{kT}} + 1}}$$

5.

The Entropy, and Energy of Electron-Gas, the Easy Way

We assume that

Energy of electrons ε_l is multiple of discrete energy units,

And that the entropy is

$$S(W) = k \log W\,,$$

And that

N_l electrons at energy ε_l are distributed between Z_l cells

The cells have one electron, or no electrons

That is, there are more cells than electrons

$$Z_l \geq N_l\,,$$

and

$$N_l \varepsilon_l = Z_l \overline{\varepsilon}_l\,.$$

Then

5.1 The following are equivalent

- The average energy of the electron-gas per unit volume, per mode l is

$$\overline{\varepsilon}_l = \frac{\varepsilon_l}{e^{\frac{\varepsilon_l}{kT}} + 1}\,.$$

- The average entropy of the electron-gas per unit volume, per mode l is

$$\overline{s}_l = k\left\{\left(\frac{\overline{\varepsilon}_l}{\varepsilon_l} - 1\right)\log\left(1 - \frac{\overline{\varepsilon}_l}{\varepsilon_l}\right) - \frac{\overline{\varepsilon}_l}{\varepsilon_l}\log\frac{\overline{\varepsilon}_l}{\varepsilon_l}\right\}$$

♦

$$W_l \approx \frac{Z_l!}{N_l!\left(Z_l - N_l\right)!}$$

Proof:

$(\overline{\varepsilon}_l \Leftrightarrow \overline{s}_l)$

$$\overline{\varepsilon}_l = \frac{\varepsilon_l}{e^{\frac{\varepsilon_l}{kT}} + 1},$$

$$e^{\frac{\varepsilon_l}{kT}} + 1 = \frac{\varepsilon_l}{\overline{\varepsilon}_l},$$

$$\underbrace{\frac{1}{T}}_{\frac{\partial \overline{s}_l}{\partial \overline{\varepsilon}_l}} = \frac{k}{\varepsilon_l}\log\left(\frac{\varepsilon_l}{\overline{\varepsilon}_l} - 1\right),$$

$$\frac{\partial \overline{s}_l}{\partial \overline{\varepsilon}_l} = \frac{k}{\varepsilon_l}\log\left(\frac{\varepsilon_l}{\overline{\varepsilon}_l} - 1\right)$$

$$= \frac{k}{\varepsilon_l}\log\frac{1 - \frac{\varepsilon_l}{\overline{\varepsilon}_l}}{\frac{\varepsilon_l}{\overline{\varepsilon}_l}},$$

$$= k\left\{\frac{1}{\varepsilon_l}\log\left(1 - \frac{\overline{\varepsilon}_l}{\varepsilon_l}\right) - \frac{1}{\varepsilon_l}\log\frac{\overline{\varepsilon}_l}{\varepsilon_l}\right\}$$

$$\overline{s}_l = k\left\{\left(\frac{\overline{\varepsilon}_l}{\varepsilon_l} - 1\right)\log\left(1 - \frac{\overline{\varepsilon}_l}{\varepsilon_l}\right) - \frac{\overline{\varepsilon}_l}{\varepsilon_l}\log\frac{\overline{\varepsilon}_l}{\varepsilon_l}\right\}.\square$$

$(\overline{s}_l \Leftrightarrow W_l)$

$$\text{Since } \frac{\overline{\varepsilon}_l}{\varepsilon_l} = \frac{N_l}{Z_l},$$

$$\overline{s}_l = k\left\{\left(\frac{N_l}{Z_l} - 1\right)\log\left(1 - \frac{N_l}{Z_l}\right) - \frac{N_l}{Z_l}\log\frac{N_l}{Z_l}\right\}.$$

So the entropy of the N_l electrons per unit volume, per mode l is

$$S_l = Z_l\overline{s}_l$$

$$= k\left\{(N_l - Z_l)\left(\log[Z_l - N_l] - \log Z_l\right) - N_l\left(\log N_l - \log Z_l\right)\right\}$$

$$= k\left\{-(Z_l - N_l)\log(Z_l - N_l)\underbrace{-N_l\log Z_l} + Z_l\log Z_l - N_l\log N_l \underbrace{+N_l\log Z_l}\right\}$$

$$= k\left\{-(Z_l - N_l)\log(Z_l - N_l) + Z_l\log Z_l - N_l\log N_l\right\}$$

Using Sterling's formula $\log M! \approx M\log M - M$,

$$S_l \approx k\left\{-\log(Z_l - N_l)! - (Z_l - N_l) + \log Z_l! + Z_l - \log N_l! - N_l\right\}$$

$$= k\left\{-\log(Z_l - N_l)! + \log Z_l! - \log N_l!\right\}$$

$$= k\log\frac{Z_l!}{N_l!\left(Z_l - N_l\right)!}.$$

That is, the N_l electrons per unit volume, per mode l can be distributed among the Z_l cells in

$$W_l \approx \frac{Z_l!}{N_l!\left(Z_l - N_l\right)!}$$

ways.□

6.

The Energy and Entropy of Electron Gas, Planck's Way

We assume that

N_l electrons at energy ε_l are distributed between Z_l cells

The cells have one electron, or no electrons

That is, there are more cells than electrons

$$Z_l \geq N_l,$$

and

$$N_l \varepsilon_l = Z_l \overline{\varepsilon}_l.$$

Any of the Z_l cells may be occupied by an N_l electron with probability

$$p_l = \frac{N_l}{Z_l} = \frac{\overline{\varepsilon}_l}{\varepsilon_l}.$$

Or, may be unoccupied by an N_l electron with probability

$$1 - p_l = 1 - \frac{N_l}{Z_l} = 1 - \frac{\overline{\varepsilon}_l}{\varepsilon_l}.$$

By Planck, the average entropy per unit volume at mode l is

$$\overline{s}_l = -kp_l \log p_l - k(1 - p_l)\log(1 - p_l)$$

$$= k\left\{\left(\frac{\overline{\varepsilon}_l}{\varepsilon_l} - 1\right)\log\left(1 - \frac{\overline{\varepsilon}_l}{\varepsilon_l}\right) - \frac{\overline{\varepsilon}_l}{\varepsilon_l}\log\frac{\overline{\varepsilon}_l}{\varepsilon_l}\right\}.$$

We have seen that this entropy law is equivalent to the energy law

$$\overline{\varepsilon}_l = \frac{\varepsilon_l}{e^{\frac{\varepsilon_l}{kT}} + 1}.$$

Thus,

$$p_l = \frac{\overline{\varepsilon}_l}{\varepsilon_l} = \frac{1}{e^{\frac{\varepsilon_l}{kT}} + 1}$$

III. IDEAL GAS

7.

Boltzmann's First Approach

We consider

$$N$$

gas molecules in position space with volume

$$V,$$

and in momentum space with energy

$$U.$$

Each gas molecule has three position coordinates,

$$x, y, z,$$

three momentum coordinates,

$$p_x, p_y, p_z,$$

mass

$$m$$

and energy

$$\varepsilon = \frac{U}{N}.$$

so that

$$\frac{1}{2m}(p_x^2 + p_y^2 + p_z^2) = \varepsilon.$$

We divide the volume into cells with sides

$$\delta x = \delta y = \delta z = \delta q,$$

and with volume

$$(\delta q)^3.$$

Then

7.1 There are $\frac{V}{(\delta q)^3}$ volume cells in V

Therefore,

7.2 The Number of Microstates of the Volume is

$$\left(\frac{V}{(\delta q)^3}\right)^N.$$

The momentum space is divided into cells with sides

$$\delta p_x = \delta p_y = \delta p_z = \delta p$$

and with volume

$$(\delta p)^3.$$

Then,

7.3 The Number of Momentum Microstates is

$$\left[\frac{\sqrt{\frac{4}{3}e\pi m\varepsilon}^{\,3}}{(\delta p)^3}\right]^N$$

__Proof__: In $3N$-dimensional Momentum Space,

$$\frac{1}{2m}(p_{x_1}^2 + p_{y_1}^2 + p_{z_1}^2 + ... + p_{x_N}^2 + p_{y_N}^2 + p_{z_N}^2) = U$$

$$p_{x_1}^2 + p_{y_1}^2 + p_{z_1}^2 + ... + p_{x_N}^2 + p_{y_N}^2 + p_{z_N}^2 = 2mU$$

That is,

$$\sqrt{2mU}$$

is the radius of a sphere in $3N$-dimensional momentum space.

By [Zwill], a ball of radius R in $\mathcal{N}$-dimensional space has volume

$$V_{\mathcal{N}}(R) = \frac{\pi^{\frac{\mathcal{N}}{2}}}{\left(\frac{\mathcal{N}}{2}\right)!} R^{\mathcal{N}}$$

and surface area

$$S_{\mathcal{N}}(R) = \frac{dV_{\mathcal{N}}(R)}{dR} = \mathcal{N} \frac{\pi^{\frac{\mathcal{N}}{2}}}{\left(\frac{\mathcal{N}}{2}\right)!} R^{\mathcal{N}-1}$$

For large $\mathcal{N}$, by Stirling,

$$\log\left(\frac{\mathcal{N}}{2}\right)! \approx \frac{\mathcal{N}}{2}\log\frac{\mathcal{N}}{2} - \frac{\mathcal{N}}{2}$$

$$= \frac{\mathcal{N}}{2}\left(\log\frac{\mathcal{N}}{2} - 1\right)$$

$$= \frac{\mathcal{N}}{2}\left(\log\frac{\mathcal{N}}{2} - \log e\right)$$

$$= \frac{\mathcal{N}}{2}\log\frac{\mathcal{N}}{2e}$$

$$= \log\left(\frac{\mathcal{N}}{2e}\right)^{\frac{\mathcal{N}}{2}}$$

Then,

$$\left(\frac{\mathcal{N}}{2}\right)! \approx \left(\frac{\mathcal{N}}{2e}\right)^{\frac{\mathcal{N}}{2}}$$

For $\mathcal{N} = 3N$, the surface area of a sphere of radius $\sqrt{2mU}$ is

$$S_{3N}(\sqrt{2mU}) = 3N\frac{\pi^{\frac{3N}{2}}}{\left(\frac{3N}{2}\right)!}\sqrt{2mU}^{3N-1}$$

$$\approx 3N\frac{\pi^{\frac{3N}{2}}}{\left(\frac{3N}{2e}\right)^{\frac{3N}{2}}}(2mU)^{\frac{3N-1}{2}}$$

$$= \frac{(2e\pi)^{\frac{3N}{2}}}{(3N)^{\frac{3N}{2}-1}}(2mU)^{\frac{3N-1}{2}}$$

$$\approx \left(\frac{4e\pi mU}{3N}\right)^{\frac{3N}{2}}$$

And since $U = N\varepsilon$,

$$\approx \sqrt{\tfrac{4}{3}e\pi m\varepsilon}^{3N}$$

The momentum volume of a spherical shell of thickness δp is

$$\approx \sqrt{\tfrac{4}{3}e\pi m\varepsilon}^{3N}\delta p$$

The volume of a momentum cell in the $3N$ dimensional Momentum space is

$$(\delta p)^{3N}.$$

Therefore, the number of momentum microstates is

$$\approx \frac{\sqrt{\tfrac{4}{3}e\pi m\varepsilon}^{3N}}{(\delta p)^{3N}}\delta p$$

$$\approx \left(\frac{\sqrt{\tfrac{4}{3}e\pi m\varepsilon}^{3}}{(\delta p)^{3}}\right)^{N}. \square$$

7.4 There are $\dfrac{\sqrt{\frac{4}{3}e\pi m\varepsilon}^{3}}{(\delta p)^3}$ **Momentum cells with energy** ε

7.5 The Momentum Ball with Volume $\sqrt{\frac{4}{3}e\pi m\varepsilon}^{3} = \frac{4}{3}\pi\rho^3$

has Radius $\rho = (\frac{4}{3}\pi)^{\frac{1}{6}}\sqrt{em\varepsilon}$

We define

7.6 $$(\delta q)(\delta p) \equiv h$$

7.7 The Number of Microstates of a Molecule with $\varepsilon = \dfrac{U}{N}$

is $$\frac{V}{(\delta q)^3} \times \frac{\sqrt{\frac{4}{3}e\pi m\varepsilon}^{3}}{(\delta p)^3} = \frac{1}{h^3}V\left(\tfrac{4}{3}e\pi m\frac{U}{N}\right)^{\frac{3}{2}}$$

7.8 The Number of Volume and Momentum Microstates is

$$\left[\frac{1}{h^3}V\left(\tfrac{4}{3}e\pi m\frac{U}{N}\right)^{\frac{3}{2}}\right]^N$$

7.9 The Gas with Energy U, in Volume V has Entropy

$$S(U,V) = k\log\left[\frac{1}{h^3}V\left(\frac{U}{N}\tfrac{4}{3}e\pi m\varepsilon\right)^{\frac{3}{2}}\right]^N$$

7.10 The N-molecules Gas satisfies Ideal Gas Equations

$$U = \tfrac{3}{2} NkT$$

$$PV = NkT$$

Proof:

$$S(U,V) = k\log\left[\frac{1}{h^3}V\left(\frac{U}{N}\tfrac{4}{3}e\pi m\varepsilon\right)^{\frac{3}{2}}\right]^N$$

$$= kN\left\{\log\frac{1}{h^3} + \log V + \frac{3}{2}\left[\log U - \log N + \log\tfrac{4}{3}e\pi m\varepsilon\right]\right\}$$

$$dS = \frac{dU + PdV}{T} \Rightarrow \frac{1}{\underbrace{T}_{}} = \frac{\partial S}{\partial U} = \underbrace{kN\frac{3}{2}\frac{1}{U}}_{} \Rightarrow U = \tfrac{3}{2}NkT$$

$$\frac{P}{\underbrace{T}_{}} = \frac{\partial S}{\partial V} = \underbrace{kN\frac{1}{V}}_{} \Rightarrow PV = NkT\,.\square$$

8.

Sparse Photon Gas

From Section **3**, At frequency ν.

N_ν photons $h\nu$ are distributed between Z_ν radiators

Thus,

$$U = N_\nu h\nu = Z_\nu \overline{\varepsilon}_\nu .$$

The average entropy per unit volume at frequency ν is

$$\overline{s}_\nu = \frac{S_\nu}{Z_\nu} = k\left\{\left(\frac{N_\nu}{Z_\nu}+1\right)\log\left(\frac{N_\nu}{Z_\nu}+1\right) - \frac{N_\nu}{Z_\nu}\log\frac{N_\nu}{Z_\nu}\right\}$$

A Photon Gas is **Sparse** iff $N_\nu \ll Z_\nu$

Then,

8.1 $$\boxed{S_\nu = kN_\nu \log e\frac{Z_\nu}{N_\nu}}$$

Proof: $$S_\nu = kZ_\nu\left\{\left(\frac{N_\nu}{Z_\nu}+1\right)\log\left(\frac{N_\nu}{Z_\nu}+1\right) - \frac{N_\nu}{Z_\nu}\log\frac{N_\nu}{Z_\nu}\right\}$$

$$= k\left\{\left(N_\nu + Z_\nu\right)\log\left(\frac{N_\nu}{Z_\nu}+1\right) - N_\nu\log\frac{N_\nu}{Z_\nu}\right\}$$

$$= k\left\{(N_\nu + Z_\nu)[\log(N_\nu + Z_\nu) - \log Z_\nu] - N_\nu[\log N_\nu - \log Z_\nu]\right\}$$

$$= k\{N_\nu \log(N_\nu + Z_\nu) + Z_\nu \log(N_\nu + Z_\nu)\underbrace{-N_\nu \log Z_\nu} - Z_\nu \log Z_\nu\}$$

$$+k\{-N_\nu \log N_\nu + \underbrace{N_\nu \log Z_\nu}\}$$

$$= k\Big\{P_\nu[\log(N_\nu + Z_\nu) - \log P_\nu] + Z_\nu[\log(N_\nu + Z_\nu) - \log Z_\nu]\Big\}$$

$$= kN_\nu\left\{[\log(N_\nu + Z_\nu) - \log N_\nu] + \frac{Z_\nu}{N_\nu}[\log(N_\nu + Z_\nu) - \log Z_\nu]\right\}$$

$$= kN_\nu\left\{\log\frac{N_\nu + Z_\nu}{N_\nu} + \frac{Z_\nu}{N_\nu}\log\frac{N_\nu + Z_\nu}{Z_\nu}\right\}$$

$$= kN_\nu\left\{\log\left(1 + \frac{Z_\nu}{N_\nu}\right) + \frac{Z_\nu}{N_\nu}\log\left(1 + \frac{N_\nu}{Z_\nu}\right)\right\}$$

$$\approx kN_\nu\left\{\log\frac{Z_\nu}{N_\nu} + \log\underbrace{\left(1 + \frac{N_\nu}{Z_\nu}\right)^{\frac{Z_\nu}{N_\nu}}}_{\approx e}\right\}$$

$$= kN_\nu\left\{\log\frac{Z_\nu}{N_\nu} + \log e\right\}$$

$$= kN_\nu \log e\frac{Z_\nu}{N_\nu}.\square$$

By **7.8**, The number of microstates of a photon with $h\nu = \dfrac{U}{N_\nu}$ is

$$Z_\nu = \frac{1}{h^3}V\left(\tfrac{4}{3}e\pi m\frac{U}{N_\nu}\right)^{\frac{3}{2}}$$

Thus,

$$\frac{Z_\nu}{N_\nu} = \frac{1}{h^3}\frac{V}{N_\nu}\left(\tfrac{4}{3}e\pi m\frac{U}{N_\nu}\right)^{\frac{3}{2}}$$

$$\frac{N_\nu}{Z_\nu} = h^3 \frac{N_\nu}{V}\left(\tfrac{3}{4}\frac{1}{e\pi m}\frac{N_\nu}{U}\right)^{\frac{3}{2}}.$$

8.2

$$\boxed{\overline{s}_\nu = kh^3 \frac{N_\nu}{V}\left(\tfrac{3}{4}\frac{1}{e\pi m}\frac{N_\nu}{U}\right)^{\frac{3}{2}} \log e^{\frac{5}{2}} \frac{1}{h^3}\frac{V}{N_\nu}\left(\tfrac{4}{3}\pi m\frac{U}{N_\nu}\right)^{\frac{3}{2}}}$$

Proof:

$$\overline{s}_\nu = \frac{S_\nu}{Z_\nu} = k\frac{P_\nu}{Z_\nu}\log e\frac{Z_\nu}{N_\nu}$$

$$= kh^3 \frac{N_\nu}{V}\left(\tfrac{3}{4}\frac{1}{e\pi m}\frac{N_\nu}{U}\right)^{\frac{3}{2}} \log e\frac{1}{h^3}\frac{V}{N_\nu}\left(\tfrac{4}{3}e\pi m\frac{U}{N_\nu}\right)^{\frac{3}{2}}$$

$$= kh^3 \frac{N_\nu}{V}\left(\tfrac{3}{4}\frac{1}{e\pi m}\frac{N_\nu}{U}\right)^{\frac{3}{2}} \log e^{\frac{5}{2}} \frac{1}{h^3}\frac{V}{N_\nu}\left(\tfrac{4}{3}\pi m\frac{U}{N_\nu}\right)^{\frac{3}{2}}$$

9.

Sparse Electron Gas

From Section **5**,

N_l electrons at energy ε_l are distributed between Z_l cells

There are more cells than electrons,

$$Z_l \geq N_l$$

and

$$U = N_l \varepsilon_l = Z_l \overline{\varepsilon}_l .$$

The average entropy per unit volume, per mode l is

$$\overline{s}_l = \frac{S_l}{Z_l} = k\left\{\left(\frac{N_l}{Z_l} - 1\right)\log\left(1 - \frac{N_l}{Z_l}\right) - \frac{N_l}{Z_l}\log\frac{N_l}{Z_l}\right\}$$

Electron Gas is **Sparse** iff $N_l \ll Z_l$

Then,

9.1 $$\boxed{S_l = kN_l \log\frac{Z_l}{eN_l}}$$

<u>Proof</u>: $S_l = Z_l \overline{s}_l$

$$= k\left\{(N_l - Z_l)\left(\log[Z_l - N_l] - \log Z_l\right) - N_l\left(\log N_l - \log Z_l\right)\right\}$$

$$= k\left\{-(Z_l - N_l)\log(Z_l - N_l)\underbrace{-N_l \log Z_l} + Z_l \log Z_l - N_l \log N_l \underbrace{+N_l \log Z_l}\right\}$$

$$= k\left\{-(Z_l - N_l)\log(Z_l - N_l) + Z_l \log Z_l - N_l \log N_l\right\}$$

$$= k\left\{-Z_l[\log(Z_l - N_l) - \log Z_l] + N_l[\log(Z_l - N_l) - \log N_l]\right\}$$

$$= kN_l\left\{[\log(Z_l - N_l) - \log N_l] - \frac{Z_l}{N_l}[\log(Z_l - N_l) - \log Z_l]\right\}$$

$$= kN_l\left\{\log\frac{Z_l - N_l}{N_l} - \frac{Z_l}{N_l}\log\frac{Z_l - N_l}{Z_l}\right\}$$

$$= kN_l\left\{\log\left(\frac{Z_l}{N_l} - 1\right) - \frac{Z_l}{N_l}\log\left(1 - \frac{N_l}{Z_l}\right)\right\}$$

$$= kN_l\left\{\log\underbrace{\left(\frac{Z_l}{N_l} - 1\right)}_{\approx Z_l/N_l} + \log\underbrace{\left(1 - \frac{N_l}{Z_l}\right)^{-\frac{Z_l}{N_l}}}_{\approx e^{-1}}\right\}$$

$$\approx kN_l\left\{\log\frac{Z_l}{N_l} - \log e\right\}$$

$$= kN_l\log\frac{Z_l}{eN_l}.\square$$

By **7.8**, The number of microstates of an electron with $\varepsilon_l = \frac{U}{N_l}$ is

$$Z_l = \frac{1}{h^3}V\left(\tfrac{4}{3}e\pi m\frac{U}{N_l}\right)^{\frac{3}{2}}$$

Thus,

$$\frac{Z_l}{N_l} = \frac{1}{h^3}\frac{V}{N_l}\left(\tfrac{4}{3}e\pi m\frac{U}{N_l}\right)^{\frac{3}{2}}$$

$$\frac{N_l}{Z_l} = h^3 \frac{N_l}{V}\left(\tfrac{3}{4}\frac{1}{e\pi m}\frac{N_l}{U}\right)^{\frac{3}{2}}.$$

9.2 $$\boxed{\overline{s_l} = kh^3 \frac{N_l}{V}\left(\tfrac{3}{4}\frac{1}{e\pi m}\frac{N_l}{U}\right)^{\frac{3}{2}} \log \sqrt{e}\,\frac{1}{h^3}\frac{V}{N_l}\left(\tfrac{4}{3}\pi m\frac{U}{N_l}\right)^{\frac{3}{2}}}$$

Proof: $$\overline{s}_\nu = \frac{S_l}{Z_l} = k\frac{N_l}{Z_l}\log\left(\frac{Z_l}{eN_l}\right)$$

$$= kh^3 \frac{N_l}{V}\left(\tfrac{3}{4}\frac{1}{e\pi m}\frac{N_l}{U}\right)^{\frac{3}{2}} \log \frac{1}{eh^3}\frac{V}{N_l}\left(\tfrac{4}{3}e\pi m\frac{U}{N_l}\right)^{\frac{3}{2}}.$$

$$= kh^3 \frac{N_l}{V}\left(\tfrac{3}{4}\frac{1}{e\pi m}\frac{N_l}{U}\right)^{\frac{3}{2}} \log \sqrt{e}\,\frac{1}{h^3}\frac{V}{N_l}\left(\tfrac{4}{3}\pi m\frac{U}{N_l}\right)^{\frac{3}{2}}.\square$$

10.

Boltzmann's Second Approach

The N gas molecules have

n_1 molecules with energy ε_1

n_2 molecules with energy ε_2

……………………………………

n_J molecules with energy ε_J

The number of microstates is

$$\frac{N!}{n_1!n_2!.....n_J!}$$

and the entropy of the gas is

$$S = k\log\frac{N!}{n_1!n_2!.....n_J!}$$

By Stirling approximation, for large M, $\log M! \approx M\log M - M$. So

$$S \approx k\left\{N(\log N - 1) - n_1(\log n_1 - 1) - ... - n_J(\log n_J - 1)\right\}$$

$$= k\left\{N\log N - n_1\log n_1 - ... - n_J\log n_J\right\}$$

The energy is

$$U = n_1\varepsilon_1 + n_2\varepsilon_2 + ... + n_J\varepsilon_J$$

At thermal equilibrium, the entropy has a maximum under this constraint.

We apply the Lagrange multiplier method with multiplier

$$\beta > 0,$$

to the auxiliary function

$$\Phi(n_i, \beta) = k\left\{N \log N - n_1 \log n_1 - ... - n_J \log n_J\right\} + \beta(U - n_1\varepsilon_1 - .. - n_J\varepsilon_J)$$

10.1 $$\boxed{n_i = e^{-1}e^{-\beta\varepsilon_i}}$$

Proof: The critical points are at

$$0 = \frac{\partial \Phi}{\partial n_i} = -\underbrace{\frac{\partial}{\partial n_i}(n_i \log n_i)}_{\log n_i + n_i\frac{1}{n_i}} - \beta\varepsilon_i$$

$$= -\log n_i - 1 - \beta n_i.$$

$$\log n_i = -1 - \beta\varepsilon_i$$

$$n_i = e^{-1}e^{-\beta\varepsilon_i}.\Box$$

10.2 $$S(N, U) = kN \log Ne + \frac{U}{T}$$

Proof: $S \approx k\left\{N \log N - n_1 \log n_1 - ... - n_J \log n_J\right\}$

$$= k\left\{N \log N - n_1(-1 - \beta\varepsilon_1) - ... - n_J(-1 - \beta\varepsilon_J)\right\}$$

$$= k\left\{N \log N + \underbrace{n_1 + ... + n_J}_{N} + \beta\underbrace{(\varepsilon_1 n_1 + .. + \varepsilon_J n_J)}_{U}\right\}$$

$$= k\left\{N(\log N + \log e) + \beta U\right\}$$

$$= k\{N \log Ne + \beta U\}$$

Therefore,

$$\frac{1}{\underbrace{T}_{}} = \frac{\partial S}{\partial U} = \underbrace{k\beta}_{}$$

$$\beta = \frac{1}{kT}$$

$$S(N,U) = kN\log Ne + \frac{U}{T}.\square$$

10.3 $$Ne = e^{-\frac{\varepsilon_1}{kT}} + e^{-\frac{\varepsilon_2}{kT}} + ... + e^{-\frac{\varepsilon_J}{kT}}$$

Proof: $$Ne = n_1e + n_2e + ... + n_Je$$

$$= e^{-\beta\varepsilon_1} + e^{-\beta\varepsilon_2} + ... + e^{-\beta\varepsilon_J}$$

$$= e^{-\frac{\varepsilon_1}{kT}} + e^{-\frac{\varepsilon_2}{kT}} + ... + e^{-\frac{\varepsilon_J}{kT}}.\square$$

10.4 $$e^{-\frac{\varepsilon_1}{kT}} + e^{-\frac{\varepsilon_2}{kT}} + ... + e^{-\frac{\varepsilon_J}{kT}} \approx \frac{1}{h^3}V\sqrt{2\pi mkT}^3$$

Proof:

$$(e^{-\frac{\varepsilon_1}{kT}} + e^{-\frac{\varepsilon_2}{kT}} + ... + e^{-\frac{\varepsilon_J}{kT}})h^3 =$$

$$= (e^{-\frac{\varepsilon_1}{kT}} + e^{-\frac{\varepsilon_2}{kT}} + ... + e^{-\frac{\varepsilon_J}{kT}})(\delta q)^3(\delta p)^3$$

$$= (e^{-\frac{\varepsilon_1}{kT}} + e^{-\frac{\varepsilon_2}{kT}} + ... + e^{-\frac{\varepsilon_J}{kT}})(\delta x)(\delta y)(\delta z)(\delta p_x)(\delta p_y)(\delta p_z)$$

The energy of a gas molecule is

$$\varepsilon = \frac{1}{2m}(p_x^2 + p_y^2 + p_z^2)$$

$$e^{-\frac{\varepsilon}{kT}} = e^{-\frac{1}{kT}\frac{1}{2m}(p_x^2+p_y^2+p_z^2)}$$

And we replace the sum by integrating over x, y, z, p_x, p_y, p_z

$$\underbrace{\int_x dx \int_y dy \int_z dz}_{V} \int_{p_x} e^{-\frac{1}{kT}\frac{1}{2m}p_x^2} dp_x \int_{p_y} e^{-\frac{1}{kT}\frac{1}{2m}p_x^2} dp_y \int_{p_z} e^{-\frac{1}{kT}\frac{1}{2m}p_x^2} dp_z =$$

With the change of integration variable

$$\xi = \frac{1}{\sqrt{2mkT}}\, p$$

Each integral is

$$\sqrt{2mkT} \int_{\xi=-\infty}^{\xi=\infty} e^{-\xi^2} d\xi = \sqrt{2\pi mkT}$$

Therefore,

$$(e^{-\frac{\varepsilon_1}{kT}} + e^{-\frac{\varepsilon_2}{kT}} + ... + e^{-\frac{\varepsilon_J}{kT}})h^3 \approx V\sqrt{2\pi mkT}^3$$

$$e^{-\frac{\varepsilon_1}{kT}} + e^{-\frac{\varepsilon_2}{kT}} + ... + e^{-\frac{\varepsilon_J}{kT}} \approx \frac{1}{h^3} V\sqrt{2\pi mkT}^3 .\square$$

10.5 $$S(U,V) \approx kN \log \frac{1}{h^3} V\sqrt{2\pi mkT}^3 + \frac{U}{T}$$

Proof: $S(V,U) \approx kN \log Ne + \dfrac{U}{T}$

$$= kN \log(e^{-\frac{\varepsilon_1}{kT}} + e^{-\frac{\varepsilon_2}{kT}} + ... + e^{-\frac{\varepsilon_J}{kT}}) + \frac{U}{T}$$

$$\approx kN \log \frac{1}{h^3} V\sqrt{2\pi mkT}^3 + \frac{U}{T}$$

10.6 The N-molecules Gas satisfies the Ideal Gas Equation

$$PV = NkT$$

Proof:

$$S(U,V) \approx kN \log \frac{1}{h^3} V \sqrt{2\pi mkT}^{\,3} + \frac{U}{T}$$

$$= kN \left\{ \log \frac{1}{h^3} + \log V + \frac{3}{2} \log 2\pi mkT \right\} + \frac{U}{T}$$

$$dS = \frac{dU + PdV}{T} \;\Rightarrow\; \underbrace{\frac{P}{T}} = \frac{\partial S}{\partial V} = \underbrace{kN\frac{1}{V}} \;\Rightarrow\; PV = NkT\,.\square$$

10.7 The N-molecules Gas satisfies the Ideal Gas Equation

$$U = \tfrac{3}{2} NkT$$

Proof: $$\frac{U}{N} = \frac{n_1\varepsilon_1 + n_2\varepsilon_2 + ... + n_J\varepsilon_J}{n_1 + n_2 + ... + n_J}$$

$$= \frac{e^{-1}e^{-\beta\varepsilon_1}\varepsilon_1 + e^{-1}e^{-\beta\varepsilon_2}\varepsilon_2 + ... + e^{-1}e^{-\beta\varepsilon_J}\varepsilon_J}{e^{-1}(e^{-\beta\varepsilon_1} + e^{-\beta\varepsilon_2} + ... + e^{-\beta\varepsilon_J})}$$

$$= \frac{e^{-\beta\varepsilon_1}\varepsilon_1 + e^{-\beta\varepsilon_2}\varepsilon_2 + ... + e^{-\beta\varepsilon_J}\varepsilon_J}{e^{-\beta\varepsilon_1} + e^{-\beta\varepsilon_2} + ... + e^{-\beta\varepsilon_J}}$$

$$= -\frac{\partial}{\partial\beta} \log(e^{-\beta\varepsilon_1} + e^{-\beta\varepsilon_2} + ... + e^{-\beta\varepsilon_J})$$

$$\approx -\frac{\partial}{\partial\beta} \log \frac{1}{h^3} V \sqrt{\frac{2\pi m}{\beta}}^{\,3}$$

$$= -\frac{\partial}{\partial\beta} \left\{ \log \frac{1}{h^3} V + \frac{3}{2} \log 2\pi m - \frac{3}{2} \log \beta \right\}$$

$$= \frac{3}{2}\frac{1}{\beta} = \frac{3}{2} kT$$

$$\Rightarrow U = \frac{3}{2} NkT\,.\square$$

11.

The Entropy of Ideal Gas

We show that the entropy of ideal gas follows easily from Planck's radiation Law:

By Planck's Radiation Law, the average energy of radiation per unit volume, at frequency ν is

$$\overline{\varepsilon}_{\nu} = \frac{h\nu}{e^{\frac{h\nu}{kT}} - 1}.$$

By the equivalence between energy and mass,

$$\varepsilon = mc^2,$$

the photon, $h\nu$ has mass μ_{ν} so that

$$h\nu = \mu_{\nu}c^2.$$

Therefore, Planck's radiation law can be written as

$$\overline{\varepsilon}_{\nu} = \frac{\mu_{\nu}c^2}{e^{\frac{\mu_{\nu}c^2}{kT}} - 1},$$

$$\frac{\overline{\varepsilon}_{\nu}}{c^2} = \frac{\mu_{\nu}}{e^{\frac{\mu_{\nu}c^2}{kT}} - 1}.$$

Denoting

$$\frac{\overline{\varepsilon}_{\nu}}{c^2} \equiv \overline{\mu}_{\nu},$$

we obtain an equivalent mass Law:

It says that the average mass per unit volume, at frequency ν is

$$\bar{\mu}_\nu = \frac{\mu_\nu}{e^{\frac{\mu_\nu c^2}{kT}} - 1}.$$

If the mass quantum is the mass of an atom of an ideal gas,

$$m,$$

The average mass per unit volume is

$$\bar{m} = \frac{m}{e^{\frac{mc^2}{kT}} - 1}.$$

Then,

11.1

The average entropy of the ideal gas per unit volume is

$$\boxed{\bar{s} = k\left\{\left(\frac{\bar{m}}{m} + 1\right)\log\left(\frac{\bar{m}}{m} + 1\right) - \frac{\bar{m}}{m}\log\frac{\bar{m}}{m}\right\}}.$$

12.

Condensation of Ideal Gas

The statistics of molecules is the same as photons with energy $h\nu$

N molecules with energy U in volume V distributed in Z cells

At condensation, all the molecules are in one cell.

That is, the number of cells is

$$Z = 1.$$

12.1 At Condensation, the Entropy Vanishes

Proof: The Number of microstates is

$$W_1 = \frac{(N+Z-1)!}{(N)!(Z-1)!} = \frac{(N])!}{(N)!} = 1$$

And the Entropy is

$$S_1 = k\log W_1 = k\log 1 = 0.\Box$$

By the Third Law of Thermodynamics,

$$T \to 0 \quad \Rightarrow \quad \mathrm{S} \to 0.$$

But

12.2 Condensation Temperature is Higher than Zero.

Proof: The Volume occupied by the molecules is

$$V_0,$$

And the Energy is

$$U_0.$$

By **7.8**, the number of microstates of

$$N$$

molecules with energy

$$U$$

in volume

$$V$$

is

$$Z = \frac{1}{h^3} V \left(\tfrac{4}{3} e\pi m \frac{U}{N} \right)^{\frac{3}{2}}$$

At condensation,

$$1 = \frac{1}{h^3} V_0 \left(\tfrac{4}{3} e\pi m \frac{U_0}{N} \right)^{\frac{3}{2}}$$

Dividing the first equation by the second,

$$Z = \frac{VU^{\frac{3}{2}}}{V_0 U_0^{\frac{3}{2}}}$$

$$U_0 = \left(\frac{V}{ZV_0} \right)^{\frac{2}{3}} U$$

For N molecules of ideal gas, $U = \frac{3}{2} NkT$.

Hence,

$$U_0 = \left(\frac{V}{ZV_0} \right)^{\frac{2}{3}} \frac{3}{2} NkT \neq 0.$$

That is, at condensation the gas energy does not vanish.

Thus, the condensation temperature is higher than zero.□

IV. BOSE-EINSTEIN

13.

The Count of the Number of the Radiating Oscillators,

The number of photon radiating oscillators per unit volume at frequencies between ν, and $\nu + d\nu$ was computed by Rayleigh as the number of standing waves per unit volume in the modes between ν, and $\nu + d\nu$. It is

$$N_{\nu} = \frac{8\pi}{c^3}\nu^2 .$$

Bose and Einstein attempted to obtain it from momentum considerations, and failed:

The momentum of a photon $h\nu$ is

$$p = \left|\vec{p}\right| = \frac{h\nu}{c},$$

where

$$h \text{ is in } \text{Joule} \times \text{sec} = \text{Newton} \times \text{meter} \times \text{sec}$$

In momentum space,

$$(p_x, p_y, p_z),$$

$\frac{h\nu}{c}$ is on the surface of the sphere

$$p_x^2 + p_y^2 + p_z^2 = \frac{h^2\nu^2}{c^2}.$$

Then, for each of its two polarizations, the momentum of the radiation per unit volume in the spherical shell between

$$\nu\text{, and } \nu + d\nu\text{,}$$

is

$$4\pi p^2 dp = 4\pi\frac{h^2\nu^2}{c^2}\frac{h}{c}d\nu = h^3 4\pi\frac{\nu^2}{c^3}d\nu\,.$$

And, for the two possible polarization it is

$$h^3 8\pi\frac{\nu^2}{c^3}d\nu\,.$$

So there are

$$8\pi\frac{\nu^2}{c^3}$$

cells of size

$$h^3$$

per unit volume in the spherical shell between

$$\nu\text{, and } \nu + d\nu\,.$$

For the possible frequencies

$$\nu_1, \nu_2, \nu_3, \ldots., \nu_l, \ldots,$$

there are

$$8\pi\frac{\nu_l^2}{c^3}$$

cells of size h^3 per unit volume in the spherical shell between

$$\nu_l\text{, and } \nu_l + d\nu_l\,.$$

It is not clear why Bose and Einstein believed that the number of cells of size h^3 equals N_ν = The number of radiating oscillators per unit volume at frequencies between ν, and $\nu + d\nu$.

14.

The Energy, and Entropy of Photon-Gas, Boltzmann Way

In the following we present the derivation of entropy following Bose, in the detail that was beyond Bose and Einstein.

14.1 The Derivation

For the possible frequencies

$$\nu_1, \nu_2, \nu_3, ..., \nu_l, \cdots,$$

$N_{\nu_l}^{(0)}$ is the number of particles with no energy,

$N_{\nu_l}^{(1)}$ is the number of particles with energy $h\nu_l$,

$N_{\nu_l}^{(2)}$ is the number of particles with energy $2h\nu_l$,

……………………………………………………………………

$$N_{\nu_l} = N_{\nu_l}^{(0)} + N_{\nu_l}^{(1)} + N_{\nu_l}^{(2)} + ...,$$

For each $l = 1, 2, 3, ...,$

the N_{ν_l} particles per unit volume in the spherical shell between ν_l and $\nu_l + d\nu_l$, can be arranged in

$$\frac{N_{\nu_l}!}{N_{\nu_l}^{(0)}!N_{\nu_l}^{(1)}!N_{\nu_l}^{(2)}!...}$$

ways.

Thus, all the particles per unit volume can be arranged in

$$w=\frac{N_{\nu_1}!}{N_{\nu_1}^{(0)}!N_{\nu_1}^{(1)}!N_{\nu_1}^{(2)}!...}\times\frac{N_{\nu_2}!}{N_{\nu_2}^{(0)}!N_{\nu_2}^{(1)}!N_{\nu_2}^{(2)}!...}\times\frac{N_{\nu_3}!}{N_{\nu_3}^{(0)}!N_{\nu_3}^{(1)}!N_{\nu_3}^{(2)}!...}\times...$$

ways.

The entropy per volume element is

$$s=k\log w=k\sum_{l=1}^{l=l_{\max}}\log(N_{\nu_l}!)-k\sum_{l=1}^{l=l_{\max}}\sum_{j=0}^{j=j_{\max}}\log(N_{\nu_l}^{j}!),$$

where k is Entropy Constant.

By Sterling's formula $\log M!\approx M\log M-M$,

$$s\approx k\sum_{l=1}^{l=l_{\max}}(n_l\log N_{\nu_l}-N_{\nu_l})-k\sum_{l=1}^{l=l_{\max}}\sum_{j=0}^{j=j_{\max}}(N_{\nu_l}^{(j)}\log N_{\nu_l}^{(j)}-N_{\nu_l}^{(j)})$$

$$=k\sum_{l=1}^{l=l_{\max}}N_{\nu_l}\log N_{\nu_l}-k\sum_{l=1}^{l=l_{\max}}\sum_{j=0}^{j=j_{\max}}N_{\nu_l}^{(j)}\log N_{\nu_l}^{(j)}.$$

The number of $h\nu_l$ per unit volume is

$$N_{\nu_l}^{(1)}+2N_{\nu_l}^{(2)}+3N_{\nu_l}^{(3)}+...=\sum_{j=0}^{\infty}jN_{\nu_l}^{(j)}.$$

Therefore, the radiation energy per unit volume is

$$u=\sum_{l=1}^{l=\infty}h\nu_l\sum_{j=0}^{j=\infty}jN_{\nu_l}^{(j)}.$$

At thermal equilibrium, the entropy has a maximum under the constraint

$$N_{\nu_l} = \sum_{j=0}^{\infty} N_{\nu_l}^{(j)}, \quad l = 1,2,3,...,$$

and the constraint

$$u = \sum_{l=1}^{l=\infty} h\nu_l \sum_{j=0}^{j=\infty} jN_{\nu_l}^{(j)}.$$

We apply the Lagrange multiplier method with multipliers

$$\lambda_1, \lambda_2, \lambda_3, ..., \lambda_l, ...\lambda_{l_{\max}},$$

and

$$\beta > 0,$$

to the auxiliary function

$$F(N_{\nu_l}^{(j)}, \lambda_l, \beta) = \sum_{l=1}^{l=\infty} N_{\nu_l} \log N_{\nu_l} - \sum_{l=1}^{l=\infty}\sum_{j=0}^{j=\infty} N_{\nu_l}^{(j)} \log N_{\nu_l}^{(j)}$$

$$+\sum_{l=1}^{l=\infty} \lambda_l (N_{\nu_l} - \sum_{j=0}^{j=\infty} N_{\nu_l}^{(j)}) + \beta(u - \sum_{l=1}^{l=\infty} h\nu_l \sum_{j=0}^{j=\infty} jN_{\nu_l}^{(j)}).$$

The critical points are at

$$0 = \frac{\partial F}{\partial N_{\nu_l}^{(j)}} = \underbrace{-\frac{\partial}{\partial N_{\nu_l}^{(j)}}\left(N_{\nu_l}^{(j)} \log N_{\nu_l}^{(j)}\right)}_{\log N_{\nu_l}^{(j)} + N_{\nu_l}^{(j)} \frac{1}{N_{\nu_l}^{(j)}}} - \lambda_l - \beta jh\nu_l,$$

$$= -\log N_{\nu_l}^{(j)} - 1 - \lambda_l - \beta jh\nu_l.$$

$$\Rightarrow \qquad \log N_{\nu_l}^{(j)} = -1 - \lambda_l - \beta jh\nu_l$$

$$N_{\nu_l}^{(j)} = e^{-1-\lambda_l} e^{-j\beta h\nu_l}$$

$$0 = \frac{\partial F}{\partial \lambda_l} = N_{\nu_l} - \sum_{j=0}^{j=\infty} N_{\nu_l}^{(j)} \quad \Rightarrow \qquad N_{\nu_l} = \sum_{j=0}^{\infty} N_{\nu_l}^{(j)},$$

$$0 = \frac{\partial F}{\partial \beta} = u - \sum_{l=1}^{l=\infty} h\nu_l \sum_{j=0}^{j=\infty} jN_{\nu_l}^{(j)} \Rightarrow \; u = \sum_{l=1}^{l=\infty} h\nu_l \sum_{j=0}^{j=\infty} jN_{\nu_l}^{(j)}$$

Hence,

$$N_{\nu_l} = e^{-1-\lambda_l} \sum_{j=0}^{\infty} e^{-j\beta h\nu_l}$$

$$= e^{-1-\lambda_l} \frac{1}{1 - e^{-\beta h\nu_l}}$$

And

$$\log N_{\nu_l} = -1 - \lambda_l - \log(1 - e^{-\beta h\nu_l}).$$

At the critical point,

$$\sum_{j=0}^{j=\infty} jN_{\nu_l}^{(j)} = e^{-1-\lambda_l} \sum_{j=0}^{j=\infty} je^{-j\beta h\nu_l}.$$

Denoting

$$\xi \equiv \beta h\nu_l,$$

$$\sum_{j=0}^{j=\infty} jN_{\nu_l}^{(j)} = e^{-1-\lambda_l} \sum_{j=0}^{j=\infty} je^{-j\xi}$$

Substituting

$$e^{-1-\lambda_l} = N_{\nu_l}(1 - e^{-\beta h\nu_l}) = N_{\nu_l}(1 - e^{-\xi}),$$

$$\sum_{j=0}^{j=\infty} jN_{\nu_l}^{(j)} = N_{\nu_l}(1 - e^{-\xi}) \sum_{j=0}^{j=\infty} je^{-j\xi}$$

$$= N_{\nu_l}(1 - e^{-\xi}) \sum_{j=0}^{\infty} \left(-\frac{d}{d\xi} e^{-j\xi}\right)$$

The series

$$1 + e^{-\xi} + e^{-2\xi} + e^{-3\xi} + \ldots \text{ converges uniformly to } \frac{1}{1 - e^{-\xi}},$$

and can be differentiated term by term with respect to ξ. Thus,

$$\sum_{j=0}^{j=\infty} \left(-\frac{d}{d\xi} e^{-j\xi}\right) = -\frac{d}{d\xi} \sum_{j=0}^{j=\infty} e^{-j\xi},$$

$$= -\frac{d}{d\xi} \frac{1}{1 - e^{-\xi}}$$

$$= \frac{e^{-\xi}}{(1 - e^{-\xi})^2}$$

Therefore,

$$\sum_{j=1}^{\infty} j N_{\nu_l}^{(j)} = N_{\nu_l} (1 - e^{-\xi}) \frac{e^{-\xi}}{(1 - e^{-\xi})^2}$$

$$= N_{\nu_l} \frac{1}{e^{\xi} - 1}$$

$$= N_{\nu_l} \frac{1}{e^{\beta h \nu_l} - 1}. \qquad (10)$$

Therefore,

$$u = \sum_{l=1}^{l=\infty} h\nu_l \sum_{j=0}^{j=\infty} j N_{\nu_l}^{(j)}$$

$$= \sum_{l=1}^{\infty} N_{\nu_l} h\nu_l \frac{1}{e^{\beta h \nu_l} - 1}. \quad (11)$$

Hence,

$$s \approx k \sum_{l=1}^{l=\infty} N_{\nu_l} \log N_{\nu_l} - k \sum_{l=1}^{l=\infty} \sum_{j=0}^{j=\infty} N_{\nu_l}^{(j)} (-1 - \lambda_l - \beta j h \nu_l).$$

$$= k\sum_{l=1}^{l=\infty} N_{\nu_l}\log N_{\nu_l} + k\sum_{l=1}^{l=\infty}(1+\lambda_l)\underbrace{\sum_{j=0}^{j=\infty} N_{\nu_l}^{(j)}}_{N_{\nu_l}} + k\beta\sum_{l=1}^{l=\infty} h\nu_l \sum_{j=0}^{j=\infty} jN_{\nu_l}^{(j)}$$

$$= k\sum_{l=1}^{l=\infty} N_{\nu_l}\underbrace{(\log N_{\nu_l} + 1 + \lambda_l)}_{\log\frac{1}{1-e^{-\beta h\nu_l}}} + k\beta\underbrace{\sum_{l=1}^{l=\infty} h\nu_l \sum_{j=0}^{j=\infty} jN_{\nu_l}^{(j)}}_{u}.$$

$$= k\sum_{l=0}^{\infty} N_{\nu_l}\log\frac{1}{1-e^{-\beta h\nu_l}} + k\beta u$$

Hence,

$$\frac{1}{T} = \frac{\partial s}{\partial u} = k\beta.$$

That is, at the critical point

$$\beta = \frac{1}{kT},$$

and β is positive as required.

Then,

$$s = k\sum_{l=0}^{\infty} N_{\nu_l}\log\frac{1}{1-e^{-h\nu_l/kT}} + \frac{u}{T}$$

is the entropy at the equilibrium.

At the attained thermodynamic equilibrium

$$u = \sum_{l=0}^{\infty} N_{\nu_l}\frac{h\nu_l}{e^{h\nu_l/kT}-1} = \sum_{l=0}^{\infty} N_{\nu_l}\overline{\varepsilon_{\nu_l}}.$$

Then, the radiation energy density per unit volume between ν_l, and $\nu_l + d\nu_l$ is

$$u_{\nu_l} = N_{\nu_l} \frac{h\nu_l}{e^{h\nu_l/kT} - 1} = 8\pi \frac{\nu_l^2}{c^3} \frac{h\nu_l}{e^{h\nu_l/kT} - 1}$$

Therefore,

$$\overline{\varepsilon}_{\nu_l} = \frac{u_{\nu_l}}{N_{\nu_l}} = \frac{h\nu_l}{e^{h\nu_l/kT} - 1}$$

$$e^{\frac{h\nu_l}{kT}} - 1 = \frac{h\nu_l}{\overline{\varepsilon}_{\nu_l}},$$

$$\underbrace{\frac{1}{T}}_{\frac{\partial \overline{s}_{\nu_l}}{\partial \overline{\varepsilon}_{\nu_l}}} = \frac{k}{h\nu_l} \log\left(\frac{h\nu_l}{\overline{\varepsilon}_{\nu_l}} + 1 \right),$$

$$\frac{\partial \overline{s}_{\nu_l}}{\partial \overline{\varepsilon}_{\nu_l}} = \frac{k}{h\nu_l} \log\left(\frac{h\nu_l}{\overline{\varepsilon}_{\nu_l}} + 1 \right),$$

$$\overline{s}_{\nu_l} = k \left\{ \left(\frac{\overline{\varepsilon}_{\nu_l}}{h\nu_l} + 1 \right) \log\left(\frac{\overline{\varepsilon}_{\nu_l}}{h\nu_l} + 1 \right) - \frac{\overline{\varepsilon}_{\nu_l}}{h\nu_l} \log \frac{\overline{\varepsilon}_{\nu_l}}{h\nu_l} \right\}. \square$$

14.2 The Bose-Einstein

Bose and Einstein derivation did not elucidate the entropy.

In 1901, Planck showed the necessity of the quantum hypothesis in order to derive a formula for electromagnetic radiation that fits the measurements.

This crucial accomplishment is taken for granted by both Bose and Einstein.

They both show ignorance of Planck discovery of the formula for the probabilistic entropy

$$s = k \log w,$$

where the entropy constant k was defined and determined by Planck.

Bose and Einstein do not know the difference between

$$8\pi \frac{\nu_l^2}{c^3}, \text{ and } 8\pi \frac{\nu_l^2}{c^3} h^3.$$

$$\text{where } h^3 = 291 \times 10^{-102} \approx 10^{-100}$$

Do not have a clue about the meaning of an infinitesimal:

They write in several spots in their papers

"We obtain the number of cells corresponding to $d\nu$ as

$$8\pi V \frac{\nu^2}{c^3} d\nu \text{"}$$

The closest number to that is ZERO

They do not distinguish between the integer number of modes

$$N_{\nu_l}^{(j)},$$

and their probabilities

$$\frac{N_{\nu_l}^{(j)}}{N_{\nu_l}}$$

which are fractions.

Bose claims that every writing on Planck's radiation law before Bose is logically flawed.

But he knows not of one example that substantiates his claims.

This derivation supplied the theory for Einstein's condensation.

That is, that at very low temperatures molecules get stuck together.

15.

The Bose-Einstein Condensation

In [Einstein, p.90], Einstein claimed that for the entropy

> *"...One has*
>
> $$S = -k\sum_{s=1}^{s=\infty}\log\left(1-e^{-c\frac{s^{2/3}}{kT}}\right)+\frac{\bar{E}}{T}. \quad \textbf{(25)}$$
>
> *One can write the sum as an integral, and recast it by partial integration, to obtain*
>
> $$-\sum_{s=1}^{s=\infty}\log\left(1-e^{-c\frac{s^{2/3}}{kT}}\right) = \int_{s=0}^{s=\infty} s\frac{1}{e^{c\frac{s^{2/3}}{kT}}-1}\frac{2}{3}c\frac{s^{-1/3}}{kT}ds."$$

We do not know of any way to substantiate this equality between the discrete sum of numbers where

$$s = 1, 2, 3, \ldots.$$

and the integral, a continuous sum of infinitesimals where

$$s = \text{ any non-negative real number}$$

The approximation of a sum with an integral is common in Statistical Mechanics.

But we saw no one text that derived the condensation following Einstein's claim above.

Nevertheless, the condensation follows from our analysis above.

From section **14**,

$$N_{\nu_l} = e^{-1-\lambda_l} \frac{1}{1-e^{-\beta h\nu_l}}$$

$$= \frac{1}{e^{1+\lambda_l}} \frac{1}{1-e^{-\frac{h\nu_l}{kT}}}$$

By **12.2**, the condensation temperature T_{c} is higher than zero. So

$$\frac{1}{T_c} \neq 0$$

But the energy of a molecule is very close the zero.

$$\nu_l \approx 0$$

$$\frac{h}{kT_c}\nu_l \approx 0$$

$$e^{-\frac{h\nu_l}{kT}} \approx e^0 = 1$$

$$1-e^{-\frac{h\nu_l}{kT_c}} \approx 0$$

Therefore,

N_{ν_l} is indefinitely large

That is, the particles pile into the low energy state.

16.

Condensation and Atom Optics

Condensation takes place at very low temperature, with vanishing kinetic energies. Namely, the molecules don't move so much

So how can these molecules be used to carry a message?

This is what Atom Optics claims to do:

According to the Wikipedia[3], there were claims about holography and interferometry with atoms, as late as 2011.

The Wikipedia article does not have more recent references.

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[3] https://en.wikipedia.org/wiki/Atom_optics

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