Quantum statistics of ideal gases

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Nov. 14, 2014

Classic and Quantum statistics

- Classical Statistics:
  - Maxwell – Boltzmann statistics (MB)
- Quantum Statistics:
  - Bose – Einstein statistics (BE)
  - Fermi – Dirac statistics (FD)

Gas Model: N particles with volume V, Q_i (all coordinates), s_i (state index)

$$\left\{ s_1, s_2, \cdots, s_N \right\}$$

$$\psi = 0$$

Symmetry Requirement

- MB Statistics:
  - no requirement, particles are distinguishable
- BE Statistics:
  - Symmetric Ψ, indistinguishable particle with integral spin

$$\psi\left(\cdots Q_j \cdots Q_i \cdots\right) = \psi\left(\cdots Q_i \cdots Q_j \cdots\right)$$

- FD Statistics:
  - Symmetric Ψ, indistinguishable particle with half-integral spin

$$\psi\left(\cdots Q_j \cdots Q_i \cdots\right) = -\psi\left(\cdots Q_i \cdots Q_j \cdots\right)$$

- FD Statistics:

$$\psi\left(\cdots Q_j \cdots Q_i \cdots\right) = -\psi\left(\cdots Q_i \cdots Q_j \cdots\right)$$

If Q_i, Q_j in the same state, then

$$\psi\left(\cdots Q_j \cdots Q_i \cdots\right) = \psi\left(\cdots Q_i \cdots Q_j \cdots\right)$$

$$\psi = 0$$

Pauli exclusion principle

Example

1	2	3
AB	...	...
...	AB	...
...	...	AB
A	B	...
B	A	...
A	...	B
B	...	A
...	A	B
...	B	A

MB

1	2	3
AA	...	...
...	AA	...
...	...	AA
A	A	...
A	...	A
...	A	A

BE

1	2	3
A	A	...
A	...	A
...	A	A

FD

Formulation of statistical problem

$$E_R = n_1\varepsilon_1 + n_2\varepsilon_2 + n_3\varepsilon_3 + \cdots = \sum_r n_r\varepsilon_r$$

$$\sum_r n_r = N$$

$$Z = \sum_R e^{-\beta E_R} = \sum_R e^{-\beta\left(n_1\varepsilon_1 + n_2\varepsilon_2 + \cdots\right)}$$

$$\overline{n_r} = \frac{\sum_R n_r e^{-\beta\left(n_1\varepsilon_1 + n_2\varepsilon_2 + \cdots\right)}}{\sum_R e^{-\beta\left(n_1\varepsilon_1 + n_2\varepsilon_2 + \cdots\right)}}$$

$$\overline{n_s} = \frac{1}{Z}\sum_R \left(-\frac{1}{\beta}\frac{\partial}{\partial\varepsilon_R}\right) e^{-\beta\left(n_1\varepsilon_1 + n_2\varepsilon_2 + \cdots\right)} = -\frac{1}{\beta Z}\frac{\partial Z}{\partial\varepsilon_s} \qquad \overline{n_s} = -\frac{1}{\beta}\frac{\partial \ln Z}{\partial\varepsilon_s}$$

MB Statistics

$$Z = \sum_R e^{-\beta(n_1\varepsilon_1 + n_2\varepsilon_2 + \cdots)}$$

$$\frac{N\,!}{n_1\,!\,n_2\,!\cdots}$$

$$Z = \sum_{n_1, n_2, \cdots} \frac{N\,!}{n_1\,!\,n_2\,!\cdots} e^{-\beta(n_1\varepsilon_1 + n_2\varepsilon_2 + \cdots)}$$

$$Z = \sum_{n_1, n_2, \cdots} \frac{N\,!}{n_1\,!\,n_2\,!\cdots} \left(e^{-\beta\varepsilon_1}\right)^{n_1} \left(e^{-\beta\varepsilon_2}\right)^{n_2} \cdots$$

$$\sum_r n_r = N$$

$$Z = \left(e^{-\beta\varepsilon_1} + e^{-\beta\varepsilon_2} + \cdots\right)^N$$

$$\ln Z = N \ln\left(\sum_r e^{-\beta\varepsilon_r}\right)$$

$$\bar{n}_s = -\frac{1}{\beta}\frac{\partial \ln Z}{\partial \varepsilon_s} = -\frac{1}{\beta} N \frac{-\beta e^{-\beta\varepsilon_s}}{\sum_r e^{-\beta\varepsilon_r}}$$

$$\bar{n}_s = N \frac{e^{-\beta\varepsilon_s}}{\sum_r e^{-\beta\varepsilon_r}}$$

Photon Statistics

$$\overline{n}_s = \frac{\sum_{n_s} n_s e^{-\beta n_s \varepsilon_s} \sum_{n1,n2,\cdots}^{(s)} e^{-\beta(n_1\varepsilon_1 + n_1\varepsilon_1 + \cdots)}}{\sum_{n_s} e^{-\beta n_s \varepsilon_s} \sum_{n1,n2,\cdots}^{(s)} e^{-\beta(n_1\varepsilon_1 + n_1\varepsilon_1 + \cdots)}}$$

$$\overline{n}_s = \frac{\sum_{n_s} n_s e^{-\beta n_s \varepsilon_s}}{\sum_{n_s} e^{-\beta n_s \varepsilon_s}} \qquad n_r = 0, 1, 2, 3, \cdots$$

$$\overline{n}_s = \frac{(-1/\beta)(\partial/\partial\varepsilon_s)\sum e^{-\beta n_s \varepsilon_s}}{\sum e^{-\beta n_s \varepsilon_s}} = -\frac{1}{\beta}\frac{\partial}{\partial\varepsilon_s}\ln\left(\sum e^{-\beta n_s \varepsilon_s}\right)$$

$$\sum_{n_s=0}^{\infty} e^{-\beta n_s \varepsilon_s} = 1 + e^{-\beta\varepsilon_s} + e^{-2n_s\varepsilon_s} + \cdots = \frac{1}{1 - e^{-\beta\varepsilon_s}}$$

$$\bar{n}_s = -\frac{1}{\beta}\frac{\partial}{\partial \varepsilon_s}\ln\left(1 - e^{-\beta\varepsilon_s}\right) = \frac{e^{-\beta\varepsilon_s}}{1 - e^{-\beta\varepsilon_s}}$$

$$\bar{n}_s = \frac{1}{e^{\beta\varepsilon_s} - 1}$$

This is called the “Planck distribution”.

FD Statistics

$$\sum_r n_r = N \qquad n_r = 0,1$$

$$Z_s\left(N\right) = \sum_{n_1, n_2, \cdots}{}^{(s)} e^{-\beta\left(n_1\varepsilon_1 + n_2\varepsilon_2 + \cdots\right)} \qquad \sum_r{}^{(s)} n_r = N$$

$$\bar{n}_s = \frac{\sum_{n_s} n_s e^{-\beta n_s \varepsilon_s}}{\sum_{n_s} e^{-\beta n_s \varepsilon_s}} \quad \Longrightarrow \quad \bar{n}_s = \frac{0 + e^{-\beta n_s \varepsilon_s} Z_s\left(N-1\right)}{Z_s\left(N\right) + e^{-\beta n_s \varepsilon_s} Z_s\left(N-1\right)}$$

$$\bar{n}_s = \frac{1}{\left[Z_s\left(N\right) / Z_s\left(N-1\right)\right] e^{\beta\varepsilon_s} + 1} \qquad \Delta N \ll N$$

$$\ln Z_s\left(N - \Delta N\right) = \ln Z_s\left(N\right) - \frac{\partial \ln Z_s}{\partial N}\Delta N = \ln Z_s\left(N\right) - \alpha_s \Delta N$$

$$Z_s\left(N - \Delta N\right) = Z_s\left(N\right) e^{-\alpha_s \Delta N}$$

$$Z_s\left(N-\Delta N\right)=Z_s\left(N\right)e^{-\alpha_s \Delta N} \qquad \alpha_s=\alpha=\frac{\partial \ln Z}{\partial N}$$

$$\bar{n}_s=\frac{1}{\left[Z_s\left(N\right)/Z_s\left(N-1\right)\right]e^{\beta\varepsilon_s}+1} \Rightarrow \bar{n}_s=\frac{1}{e^{\alpha+\beta\varepsilon_s}+1} \qquad \sum_r \bar{n}_r=N$$

$$F=-kT\ln Z \qquad \alpha=\frac{\partial \ln Z}{\partial N}=-\frac{1}{kT}\frac{\partial F}{\partial N}=-\frac{\mu}{kT}=-\beta\mu$$

$$\bar{n}_r=\frac{1}{e^{\beta\left(\varepsilon_s-\mu\right)}+1}$$

μ is the chemical potential

BE Statistics

$$\bar{n}_r = \frac{0 + e^{-\beta\varepsilon_s} Z_s\left(N-1\right) + e^{-2\beta\varepsilon_s} Z_s\left(N-2\right) + \cdots}{Z_s\left(N\right) + e^{-\beta\varepsilon_s} Z_s\left(N-1\right) + e^{-2\beta\varepsilon_s} Z_s\left(N-2\right) + \cdots}$$

$$Z_s\left(N - \Delta N\right) = Z_s\left(N\right) e^{-\alpha_s \Delta N}$$

$$\bar{n}_s = \frac{Z_s\left(N\right)\left[0 + e^{-\beta\varepsilon_s} e^{-\alpha} + 2e^{-2\beta\varepsilon_s} e^{-2\alpha} + \cdots\right]}{Z_s\left(N\right)\left[1 + e^{-\beta\varepsilon_s} e^{-\alpha} + 2e^{-2\beta\varepsilon_s} e^{-2\alpha} + \cdots\right]}$$

$$\bar{n}_s = \frac{\sum_s n_s e^{-n_s(\alpha + \beta e_s)}}{\sum_s e^{-n_s(\alpha + \beta e_s)}}$$

$$n_r = 0, 1, 2, 3, \ldots$$

$$\bar{n}_s = \frac{\sum_{n_s} n_s e^{-\beta n_s e_s}}{\sum_{n_s} e^{-\beta n_s e_s}}$$

$$\bar{n}_s = \frac{1}{e^{\alpha + \beta e_s} - 1} \qquad \bar{n}_s = \frac{1}{e^{\beta(e_s - \mu)} - 1}$$

Similar to Photon Statistics

$$\sum_r \frac{1}{e^{\alpha + \beta e_r} - 1} = N$$

Partition Function of BE

$$Z = \sum_{R} e^{-\beta(n_1 e_1 + n_2 e_2 + \cdots)} \qquad n_r = 0, 1, 2, \ldots \qquad \sum_{r} n_r = N$$

$$\sum_{N'} Z\left(N^{r}\right) e^{-\alpha N^{r}} = Z'(N) e^{-\alpha N} \Delta * N' \qquad width \Delta * N' \ll N$$

$$Z' \equiv \sum_{N'} Z\left(N'\right) e^{-\alpha N'} \qquad \ln Z\left(N\right) = \alpha N + \ln Z'$$

$$Z' = \sum_{R} e^{-\beta\left(n_1 e_1 + n_2 e_2 + \cdots\right)} e^{-\alpha\left(n_1 + n_2 + \cdots\right)}$$

$$Z' = \sum_{n_1, n_2, \ldots} e^{-(\alpha + \beta e_1) n_1 - (\alpha + \beta e_2) n_2 - \cdots}$$

$$= \left(\sum_{n_1 = 0}^{\infty} e^{-(\alpha + \beta e_1) n_1} \right) \left(\sum_{n_2 = 0}^{\infty} e^{-(\alpha + \beta e_2) n_2} \right) \cdots$$

$$= \left(\frac{1}{1 - e^{-(\alpha + \beta e_1)}} \right) \left(\frac{1}{1 - e^{-(\alpha + \beta e_2)}} \right) \cdots$$

$$Z' = \left(\frac{1}{1-e^{-(\alpha+\beta e_1)}}\right)\left(\frac{1}{1-e^{-(\alpha+\beta e_2)}}\right)\cdots$$

$$\ln Z' = -\sum_r \ln\left(1-e^{-\alpha-\beta e^r}\right)$$

$$\ln Z(N) = \alpha N + \ln Z' = \alpha N - \sum_r \ln\left(1-e^{-\alpha-\beta e_r}\right)$$

Similar, for FD distribution

$$\ln Z = \alpha N + \sum_r \ln\left(1+e^{-\alpha-\beta e_r}\right)$$

Quantum statistics in classic limit

$$\bar{n}_r = \frac{1}{e^{\alpha+\beta e_r} \pm 1} \qquad \sum_r \bar{n}_r = \sum_r \frac{1}{e^{\alpha+\beta e_r} \pm 1} = N$$

$$\mathrm{lnZ} = \alpha N \pm \sum_r \ln\left(1 \pm e^{-\alpha-\beta e_r}\right)$$

$$\bar{n}_r \ll 1 \Rightarrow e^{\alpha+\beta e_r} \gg 1 \Rightarrow \bar{n}_r = e^{-\alpha-\beta e_r}$$

$$\sum_r e^{-\alpha-\beta e_r} = e^{-\alpha} \sum_r e^{-\beta e_r} = N$$

$$e^{-\alpha} = n\left(\sum_r e^{-\beta e_r}\right)^{-1} \qquad \alpha = -\mathrm{lnN} + \ln\left(\sum_r e^{-\beta e_r}\right)$$

$$\bar{n}_r = N \frac{e^{-\beta e_r}}{\sum_r e^{-\beta e_r}}$$

Quantum statistics in classic limit

$$\mathrm{lnZ} = \alpha N \pm \sum_r \ln\left(\pm e^{-\alpha-\beta e_r}\right) = \alpha N + N$$

$$\alpha = -\mathrm{lnN} + \ln\left(\sum_r e^{-\beta e_r}\right)$$

$$\ln Z = -N \ln N + N + N \ln\left(\sum_r e^{-\beta e_r}\right)$$

$$= \ln Z_{MB} - \left(N \ln N - N\right) = \ln Z_{NB} - \ln N1$$

$$Z = \left(\frac{Z_{MB}}{N\,!}\right)$$

Z of particle in ideal gases

$$\ln Z = N\left(\ln\zeta - \ln N + 1\right)$$

$$\zeta \equiv \sum_r e^{-\beta e_r}$$

$$\varepsilon = \frac{\hbar^2}{2m}\left(\kappa_x^2 + \kappa_y^2 + \kappa_z^2\right)$$

$$\zeta = \sum_{\kappa_x,\kappa_y,\kappa_z} \exp\left[-\frac{\beta\hbar^2}{2m}\left(\kappa_x^2 + \kappa_y^2 + \kappa_z^2\right)\right]$$

$$= \left(\sum_{\kappa_x} e^{-\left(\beta\hbar^2/2m\right)\kappa_x^2}\right)\left(\sum_{\kappa_y} e^{-\left(\beta\hbar^2/2m\right)\kappa_y^2}\right)\left(\sum_{\kappa_z} e^{-\left(\beta\hbar^2/2m\right)\kappa_z^2}\right)$$

$$\kappa_x = \left(2\pi/L_x\right)n_x$$

$$\frac{\partial}{\partial\kappa_x}\left[e^{-\left(\beta\hbar^2/2m\right)\kappa_x^2}\right]\left(\frac{2\pi}{L_x}\right)$$

$$\sum_{\kappa_x=-\infty}^{\infty} e^{-\left(\beta\hbar^2/2m\right)\kappa_x^2} \approx \int_{-\infty}^{\infty} e^{-\left(\beta\hbar^2/2m\right)\kappa_x^2}\left(\frac{L_x}{2\pi}d\kappa_x\right)$$

Same Result with classical statistic

$$\zeta = \frac{V}{h^3}(2\pi m k T)^{\frac{3}{2}}$$

$$\ln Z = N\left(\ln\frac{V}{N} - \frac{3}{2}\ln\beta + \frac{3}{2}\ln\frac{2\pi m}{h^2} + 1\right)$$

$$\bar{E} = -\frac{\partial \ln Z}{\partial\beta} = \frac{3}{2}\frac{N}{\beta} = \frac{3}{2}NkT$$

$$S = k(\ln Z + \beta\bar{E}) = Nk\left(\ln\frac{V}{N} + \frac{3}{2}\ln T + \sigma_0\right)$$

$$\sigma_0 = \frac{3}{2}\ln\frac{2\pi m k}{h^2} + \frac{5}{2}$$

But h here is Planck’s constant

Black – Body Radiation

- Electromagnetic radiation
- Enclosure of V at T, equilibrium
- Absorb photon and reemitted by the wall

$$\bar{n}_s = \frac{1}{e^{\beta\epsilon_s} - 1}$$

$$\nabla^2 \mathbf{\mathcal{E}} = \frac{1}{c^2}\frac{\partial^2 \mathbf{\mathcal{E}}}{\partial t^2} \qquad \mathbf{\mathcal{E}} = A\, e^{i(\boldsymbol{\kappa}\cdot\mathbf{r} - \omega t)} = \mathbf{\mathcal{E}}_0(\mathbf{r})\, e^{-i\omega t}$$

$$\nabla \cdot \mathbf{\mathcal{E}} = 0 \qquad \boldsymbol{\kappa} \cdot \mathbf{\mathcal{E}} = 0$$

Two photon in one k

Mean number per unit volume

$$f(\boldsymbol{\kappa})\, d^3\boldsymbol{\kappa} = \frac{1}{e^{\beta\hbar\omega} - 1} \frac{d^3\boldsymbol{\kappa}}{(2\pi)^3} \qquad \kappa = \omega/c \qquad \kappa + d\kappa = (\omega + d\omega)/c$$

$$2f(\kappa)(4\pi\kappa^2\, d\kappa) = \frac{8\pi}{(2\pi c)^3} \frac{\omega^2\, d\omega}{e^{\beta\hbar\omega} - 1}$$

Mean photon density

$$\bar{u}(\omega; T)\, d\omega = [2f(\kappa)(4\pi\kappa^2\, d\kappa)](\hbar\omega) = \frac{8\pi\hbar}{c^3} f(\kappa)\omega^3\, d\omega$$

$$\bar{u}(\omega; T)\, d\omega = \frac{\hbar}{\pi^2 c^3} \frac{\omega^3\, d\omega}{e^{\beta\hbar\omega} - 1}$$

Mean energy density

$$\bar{u}(\omega; T)\, d\omega = \frac{\hbar}{\pi^2 c^3} \left(\frac{kT}{\hbar}\right)^4 \frac{\eta^3\, d\eta}{e^\eta - 1} \qquad \eta \equiv \beta\hbar\omega = \frac{\hbar\omega}{kT}$$

Wien's displacement law

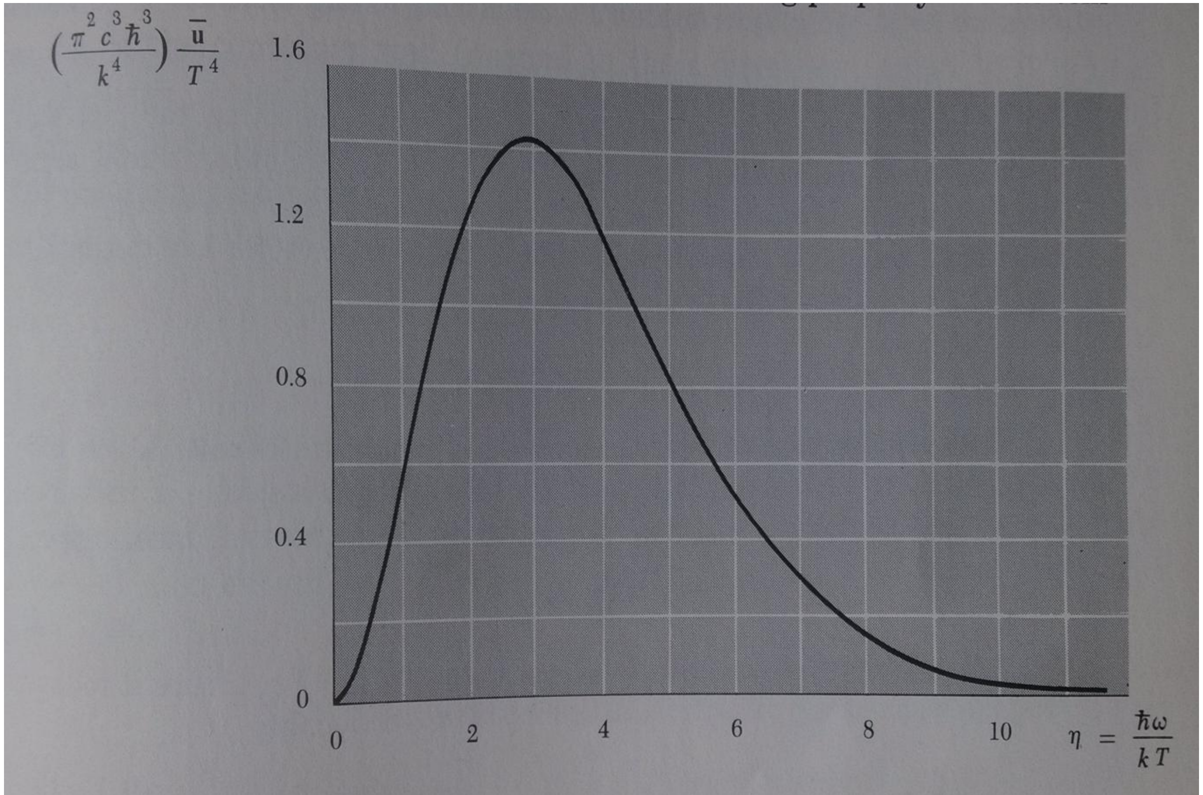

Fig. 9·13·1 The energy density $\bar{u}(\eta)$ (per unit dimensionless frequency range $d\eta$) as a function of $\eta = \hbar\omega/kT$.

$$\bar{u}(\omega; T)\, d\omega = \frac{\hbar}{\pi^2 c^3}\left(\frac{kT}{\hbar}\right)^4 \frac{\eta^3\, d\eta}{e^\eta - 1}$$

$$\frac{\hbar\bar{\omega}_1}{kT_1} = \frac{\hbar\bar{\omega}_2}{kT_2} = \bar{\eta}$$ maximum

$$\frac{\bar{\omega}_1}{T_1} = \frac{\bar{\omega}_2}{T_2}$$

$$\bar{u}_0(T) = \int_0^\infty \bar{u}(T;\omega)\, d\omega \qquad \eta \equiv \beta\hbar\omega = \frac{\hbar\omega}{kT}$$

$$\bar{u}_0(T) = \frac{\hbar}{\pi^2 c^3}\left(\frac{kT}{\hbar}\right)^4 \int_0^\infty \frac{\eta^3\, d\eta}{e^\eta - 1}$$

$$\bar{u}_0(T) \propto T^4$$

Stefan – Boltzman law

$$\bar{u}_0(T) = \frac{\pi^2}{15}\frac{(kT)^4}{(c\hbar)^3}$$