Luis Anchordoqui
Lehman College
City University of New York

Thermodynamics and Statistical Mechanics

Statistical Mechanics II
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- **Boltzmann distribution**
- **Fermi-Dirac distribution**
- **Bose-Einstein distribution**
- **Boltzmann-Maxwell distribution**
- **Statistical thermodynamics of the ideal gas**

BOLTZMANN STATISTICS

Equilibrium configuration for system of N distinguishable noninteracting particles

subject to constraints ☛ $\sum_{j=1}^{n} N_j = N$ and $\sum_{j=1}^{n} N_j \varepsilon_j = U$ (40)

# of ways of selecting N_1 particles from total of N to be place in $j = 1$ level

$$\begin{pmatrix} N \\ N_1 \end{pmatrix} = \frac{N!}{N_1!(N-N_1)!}$$

# of ways these N_1 particles can be arranged if there are g_1 quantum states

for each particle there are g_1 choices ☛ $(g_1)^{N_1}$ possibilities in all

# of ways to put N_1 particles into a level containing g_1 distinct options

$$\begin{pmatrix} N \\ N_1 \end{pmatrix} = \frac{N! g_1^{N_1}}{N_1!(N-N_1)!}$$

BOLTZMANN STATISTICS II

For $j = 2$ ☛ same situation

except that there are only $(N - N_1)$ particles remaining to deal with

$$\frac{(N-N_1)!g_2^{N_2}}{N_2!(N-N_1-N_2)!}$$

Continuing process ↴

$$\omega_{\rm B}(N_1, N_2, N_n) = \frac{N!g_1^{N_1}}{N_1!(N-N_1)!} \times \frac{(N-N_1)!g_2^{N_2}}{N_2!(N-N_1-N_2)!}$$

$$\times \frac{(N-N_1-N_2)!g_3^{N_3}}{N_3!(N-N_1-N_2-N_3)!} \cdots$$

$$= N!\frac{g_1^{N_1} g_2^{N_2} g_3^{N_3} \cdots}{N_1!N_2!N_3!\cdots} = N! \prod_{j=1}^{n} \frac{g_j^{N_j}}{N_j!}$$

We now have to maximize $\omega_{\rm B}$ subject to constraints (40)

LAGRANGE MULTIPLIERS

Maximization of $f(x,y)$ subject to constraint $\phi(x,y) = \text{constant}$

$$df = \frac{\partial f}{\partial x}dx + \frac{\partial f}{\partial y}dy = 0$$

If dx and dy were independent ☛ $\dfrac{\partial f}{\partial x} = \dfrac{\partial f}{\partial y} = 0$

However ☛ subject to constraint equation $d\phi = \dfrac{\partial \phi}{\partial x}dx + \dfrac{\partial \phi}{\partial y}dy = 0$

☟

$$\frac{\partial f/\partial x}{\partial \phi/\partial x} = \frac{\partial f/\partial y}{\partial \phi/\partial y}$$

For constant ratio α

$$\frac{\partial f}{\partial x} + \alpha\frac{\partial \phi}{\partial x} = 0 \quad \text{and} \quad \frac{\partial f}{\partial y} + \alpha\frac{\partial \phi}{\partial y} = 0$$

expressions we would get if we attempt to maximize $f + \alpha\phi$ without constraint

For n variables and two constraint relations

$$\frac{\partial f}{\partial x_i} + \alpha\frac{\partial \phi}{\partial x_i} + \beta\frac{\partial \psi}{\partial x_i} = 0, \qquad i = 1, 2, 3 \cdots n$$

BOLTZMANN DISTRIBUTION

Task ☛ find maximum of $\omega_{\rm B}$ with respect to all N that satisfy constraints (40)

In practice ☛ more convenient to maximize $\ln \omega$ than w itself

$$\ln \omega = \ln N! + \sum_{i=1}^{n} N_i \ln g_i - \sum_{i=1}^{n} \ln N_i!$$

We are concerned with $N_i \gg 1$ ☛ use Stirling's asymptotic expansion

$$\ln N! \simeq N \ln N - N + \ln \sqrt{2\pi N} + \cdots \qquad (41)$$

Neglecting relatively small last term in (41)

$$\ln \omega = \ln N! + \sum_{i=1}^{n} N_i \ln g_i - \sum_{i=1}^{n} N_i \ln N_i + \sum_i N_i \qquad (42)$$

Search for maximum of target function using Lagrange multipliers ↴

$$\frac{\partial}{\partial N_j} \left[\sum_i N_i \ln g_i - \sum_i N_i \ln N_i + \sum_i N_i \right] + \alpha \frac{\partial}{\partial N_j} \left(\sum_i N_i \right) + \beta \frac{\partial}{\partial N_j} \left(\sum_i N_i \varepsilon_i \right) = 0$$

BOLTZMANN DISTRIBUTION II

In working out the derivatives ☛ only contribution comes from terms with $j = i$

$$\ln g_j - \ln N_j - \underbrace{\frac{N_j}{N_j} + 1}_{=0} + \alpha + \beta\varepsilon_j = 0 \qquad (43)$$

For every energy level

# of particles per quantum state for equilibrium of the system

$$\frac{N_j}{g_j} = e^{\alpha + \beta\varepsilon_j} = f_j(\varepsilon_j) \qquad (44)$$

Constants α and β are related to physical properties of the system

Multiply (43) by N_j and sum over j ↴

$$\sum_j N_j \ln g_j - \sum_j N_j \ln N_j + \alpha \sum_j N_j + \beta \sum_j N_j \varepsilon_j = 0 \qquad (45)$$

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$$\sum_j N_j \ln g_j - \sum_j N_j \ln N_j = -\alpha N - \beta U \qquad (46)$$

TEMPERATURE AS A LAGRANGE MULTIPLIER

Substituting (42) ☛ $$\ln\omega = \ln N! + N - \alpha N - \beta U$$

simplifying ☛ $$\ln\omega = C - \beta U$$

Identification with Boltzmann entropy yields ☛ $$S = k\ln\omega = S_0 - k\beta U \quad (47)$$

From classical theory ☛ $$dS = \frac{dU}{dT} + \frac{PdV}{T} = \left(\frac{\partial S}{\partial U}\right)_V dU + \left(\frac{\partial S}{\partial V}\right)_U dV$$

giving ☛ $$\left(\frac{\partial S}{\partial U}\right)_V = \frac{1}{T}$$

From (47) ☛ $$\left(\frac{\partial S}{\partial U}\right)_V = -k\beta$$

giving ☛ $$\beta = -\frac{1}{kT} \quad (48)$$

Constancy of V is implied in (40) ☛ because $\epsilon_j \propto V^{-2/3}$

Luis Anchordoqui

PARTITION FUNCTION

Substituting (48) into (44) ☛ $$N_j = g_j e^{\alpha} e^{-\varepsilon_j/kT}$$

so α can be easily found from (40) ☛ $$N = \sum_j N_j = e^{\alpha} \sum_j g_j e^{-\varepsilon_j/kT}$$

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$$e^{\alpha} = \frac{N}{\sum_j g_j e^{-\varepsilon_j/kT}}$$

Boltzmann distribution becomes ☛ $$f_j = \frac{N_j}{g_j} = \frac{N \; e^{-\varepsilon_j/kT}}{\sum_j g_j e^{-\varepsilon_j/kT}}$$

partition function (German Zustandssumme) ↴

$$Z \equiv \sum_{j=1}^{n} g_j e^{-\epsilon_j/kT}$$

ENERGY LEVELS CROWDED TOGETHER VERY CLOSELY

degeneracy g_j replaced by $\rho(\varepsilon)d\varepsilon$ ☛ # of states in energy range $(\varepsilon, \varepsilon + d\varepsilon)$

correspondingly N_j replaced by $N(\varepsilon)d\varepsilon$ ☛ # of particles in range $(\varepsilon, \varepsilon + d\varepsilon)$

$$f(\varepsilon) \equiv \frac{N(\varepsilon)}{\rho(\varepsilon)} = \frac{Ne^{-\varepsilon/kT}}{\int \rho(\varepsilon)e^{-\varepsilon/kT}d\varepsilon}$$

Continuous distribution function is analogous to discrete case

$$Z = \int \rho(\varepsilon)\ e^{-\varepsilon_j/kT}d\varepsilon$$

Occupation numbers are fully determined by temperature and volume

Set of occupation numbers that maximize ω specify equilibrium macrostate

Conclusion:

Two states variables define a thermodynamic state exactly as in classical theory!

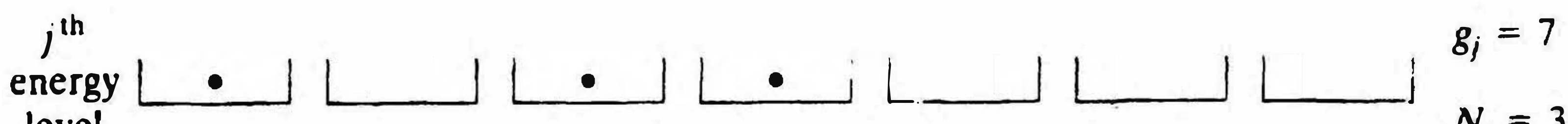
FERMI-DIRAC STATISTICS

Particles are identical (indistinguishable) and they obey Pauli's exclusion principle

half-integer spin ☛ fermions

Taking spin into account ☛ no quantum state can accept more than 1 particle

1 particle or 0 particle occupies a given state ☛ $N_j \leq g_j \; \forall j$



fermions in quantum states with energy ε_j

In determining ω for given macrostate ☛ group of g_j states divisible into subgroups

g_j are to contain 1 particle and $(g_j - N_j)$ must be unoccupied

counting problem same as coin-tossing experiment ☛ for j-th level

$$\omega_j = \frac{g_j!}{N_j!(g_j - N_j)!}$$

Total # of microstates for allowable configuration

$$\omega_{\rm FD}(N_1, N_2, \cdots, N_n) = \prod_{j=1}^{n} \frac{g_j!}{N_j!(g_j - N_j)!}$$

FERMI-DIRAC & LAGRANGE

$$\ln \omega_{\rm FD} = \sum_i \ln g_i! - \sum_i \ln N_i! - \sum_i \ln(g_i - N_i)!$$

using Stirling's

$$\ln \omega_{\rm FD} = \sum_i \left[g_i \ln g_i - g_i - N_i \ln N_i + N_i - (g - N_i) \ln(g_i - N_i) + (g_i - N_i)\right]$$

$$= \sum_i [g_i \ln g_i - N_i \ln N_i - (g_i - N_i) \ln(g_i - N_i)]$$

using $\sum_i N_i = N \qquad \sum_i N_i \varepsilon_i = U$

$$-\frac{\partial}{\partial N_j}\left[\sum_i N_i \ln N_i + \sum_i (g_i - N_i) \ln(g_i - N_i)\right] + \alpha \frac{\partial}{\partial N_j}\left(\sum_i N_i\right) + \beta \frac{\partial}{\partial N_j}\left(\sum_i N_i \varepsilon_i\right) = 0$$

Note that

$$-\frac{\partial}{\partial N_j}\left(\sum_i g_i \ln g_i\right) = 0$$

and

$$-\ln N_j - \underbrace{\frac{N_j}{N_j}}_{1} + \ln(g_j - N_j) - \underbrace{\frac{(g_j - N_j)}{(g_j - N_j)}(-1)}_{-1} = -\alpha - \beta \varepsilon_j$$

FERMI-DIRAC DISTRIBUTION

$$\ln\left(\frac{g_j}{N_j} - 1\right) = -\alpha - \beta\varepsilon_j \Rightarrow \frac{N_j}{g_j} = \frac{1}{e^{-\alpha-\beta\varepsilon_j} + 1}$$

once again ☛ $\beta = -\frac{1}{kT}$

provisionally define ☛ $\alpha = \frac{\mu}{kT}$ ↴

Fermi-Dirac distribution ☛ $f_j = \frac{N_j}{g_j} = \frac{1}{e^{(\varepsilon_j-\mu)/kT} + 1}$

continuous energy spectrum ☛ $f(\varepsilon) = \frac{1}{e^{(\varepsilon-\mu)/kT} + 1}$

BOSE-EINSTEIN STATISTICS

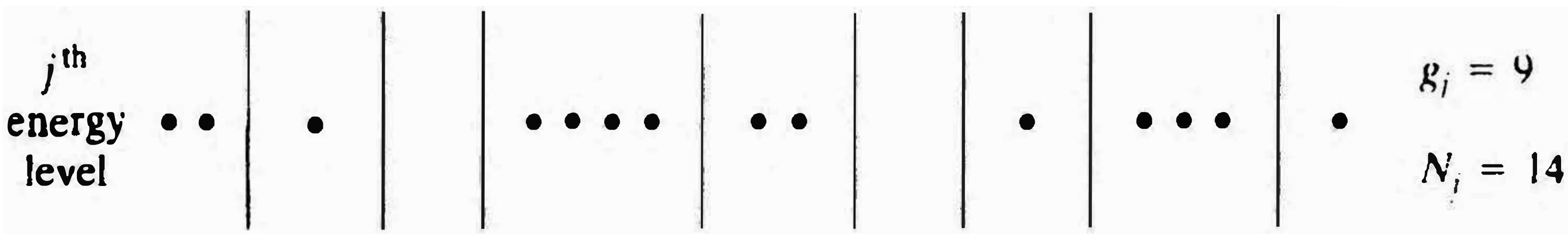
Statistics for indistinguishable particles

any number of which can occupy given quantum state

zero or integer spin ☛ bosons

Convenient to depict arrangement of N_j particles among g_j states

by $(g_j - 1)$ partitions or lines and N_j dots



bosons in quantum states with energy ε_j

new microstates obtained by shuffling lines and dots while keeping g_j and N_j fix

binomial problem of coin-tossing experiment ☛ for j-th level

$$\omega_j = \frac{(N_j + g_j - 1)!}{N_j!(g_j - 1)!}$$

Total # of microstates for allowable configuration

$$\omega_{\rm BE}(N_1, N_2, \cdots, N_n) = \prod_{j=1}^{n} \frac{(N_j + g_j - 1)!}{N_j!(g_j - 1)!}$$

BOSE-EISNTEIN & LAGRANGE

$$\ln \omega_{\rm BE} = \sum_i \ln(N_i + g_i - 1)! - \sum_i \ln N_i! - \sum_i \ln(g_i - 1)!$$

using Stirling's ↴

$$\ln \omega_{\rm BE} = \sum_i [(N_i + g_i - 1)\ln(N_i + g_i - 1) - (N_i + g_i - 1) - N_i \ln N_i + N_i - (g_i - 1)\ln(g_i - 1) + (g_i - 1)]$$

$$= \sum_i [(N_i + g_i - 1)\ln(N_i + g_i - 1) - N_i \ln N_i - (g_i - 1)\ln(g_i - 1)]$$

using ☛ $\sum_i N_i = N$ $\quad \sum_i N_i \varepsilon_i = U$

$$\frac{\partial}{\partial N_j}\left[\sum_i (N_i + g_i - 1)\ln(N_i + g_i - 1) - \sum_i N_i \ln N_i\right] + \alpha \frac{\partial}{\partial N_j}\left(\sum_i N_i\right) + \beta \frac{\partial}{\partial N_j}\left(\sum_i N_i \varepsilon_i\right) = 0$$

Note that ↴

$$\ln(N_j + g_j - 1) + \underbrace{\frac{N_j + g_j - 1}{N_j + g_j - 1}}_{1} - \ln N_j - \underbrace{\frac{N_j}{N_j}}_{1} = -\alpha - \beta \varepsilon_j$$

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BOSE-EINSTEIN DISTRIBUTION

$$\ln\left(\frac{N_j + g_j + 1}{N_j}\right) = -\alpha - \beta\varepsilon_j$$

neglecting unity compared to ☛ $$\frac{N_j}{g_i} = \frac{1}{e^{-\alpha-\beta\varepsilon_j} - 1}$$

Using $\beta = -\dfrac{1}{kT}$ and $\alpha = \dfrac{\mu}{kT}$

Bose-Eisntein distribution ☛ $$f_j = \frac{N_j}{g_i} = \frac{1}{e^{(\varepsilon_j-\mu)/kT} - 1}$$

continuous energy spectrum ☛ $$f(\varepsilon) = \frac{1}{e^{(\varepsilon-\mu)/kT} - 1}$$

MAXWELL-BOLTZMANN STATISTICS

Dilute gas ☛ for all energy levels occupations numbers are very small compared with available number of quantum states

Extremely unlikely more than 1 particle will occupy given state whether or not particles obey Pauli exclusion principle becomes irrelevant

FD and BE statistics should be approximately identical in dilute gas limit

$$\omega_{\rm FD} = \prod_j \frac{g_j!}{N_j!(g_j - N_j)!} \qquad \omega_{\rm BE} = \prod_j \frac{(g_j + N_j - 1)!}{N_j!(g_j - 1)!}$$

For $N_j \ll g_j$ ↴

$$\frac{g_j!}{(g_j - N_j)!} = \frac{g_j(g_j-1)(g_j-2)\cdots(g_j - N_j + 1)(g_j - N_j)!}{(g_j - n_j)!} \approx g_j^N$$

$$(g_j + N_j - 1)! = (g_j + N_j - 1)(g_j + N_j - 2)\cdots(g_j + N_j - N_j)(g_j - 1)!$$

$$\approx g_j^{N_j}(g_j - 1)!$$

$$\omega_{\rm FD} \approx \omega_{\rm BE} \approx \prod_j \frac{g_j^{N_j}}{N_j!}$$

MAXWELL-BOLTZMANN DISTRIBUTION

Difference between Boltzmann and Maxwell-Boltzmann statistics

Boltzmann statistics assumes distinguishable (localizable) particles

$$\omega_{\rm MB} = \prod_j \frac{g_j^{N_j}}{N_j!} \Rightarrow \omega_{\rm B} = N!\ \omega_{\rm MB}$$

Much larger Boltzmann probability includes permutation ☛ $N!$

of N identifiable particles giving rise to additional microstates

Distribution of particles among energy levels ☛ found using Lagrange multipliers

Result can be written down immediately observing that

$\omega_{\rm B}$ and $\omega_{\rm MB}$ differ only by a constant

Maxwell-Boltzmann distribution ☛ $$f_j \equiv \frac{N_j}{g_j} = \frac{N\ e^{-\varepsilon_j/kT}}{Z} \qquad (49)$$

CONNECTION BETWEEN CLASSICAL AN STATISTICAL THERMODYNAMICS

when matter is added or taken from open system change of internal energy is

$$dU = TdS - PdV + \mu dN$$

define Helmholtz function $F = U - TS$ ☛ $dF = -SdT - PdV + \mu dN$

$$\mu = \left(\frac{\partial F}{\partial N}\right)_{TV} \quad (50)$$

Calculate S and F for MB statistics ☛ $\omega_{MB} = \prod_j \frac{g_j^N}{N_j!}, \qquad \frac{N_j}{g_j} = \frac{N}{Z} e^{-\varepsilon_j/kT}$

$$S = k \ln \omega = k \left[\sum_j N_j \ln g_j - \sum_j \ln N_j!\right]$$

$$= k \left[\sum_j N_j \ln g_j - \sum_j N_j \ln N_j + \sum_j N_j\right]$$

$$= k \left[N - \sum_j N_j \ln \left(\frac{N_j}{g_j}\right)\right]$$

CONNECTION BETWEEN CLASSICAL AN STATISTICAL THERMODYNAMICS II

$$S = k\left[N - \ln N \sum_j N_j + \ln Z \sum_j N_j + \frac{1}{kT}\sum_j N_j \varepsilon_j\right]$$
$$= \frac{U}{T} + Nk(\ln Z - \ln N + 1)$$

$$F = U - TS = -NkT(\ln Z - \ln N + 1)$$

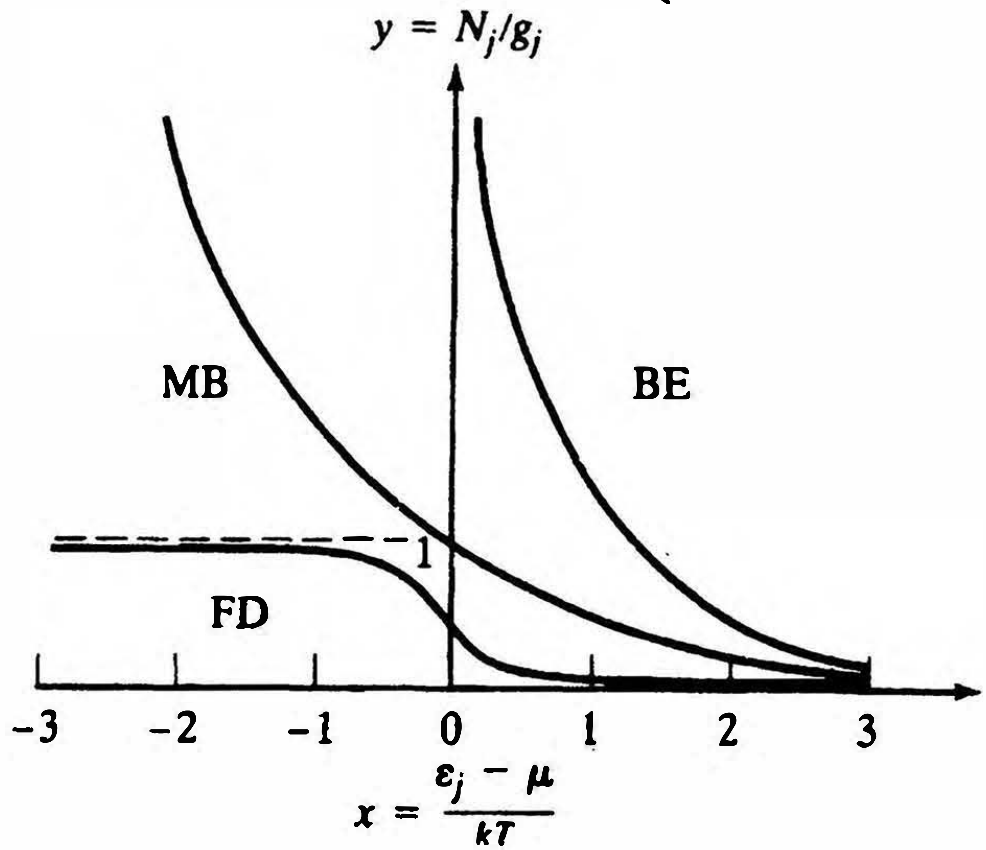
Using (50) ☛ $$\mu = -kT(\ln Z - \ln N + 1) + \frac{nkT}{N}$$
$$= kT \ln\left(\frac{N}{Z}\right)$$

$$\frac{N}{Z} = e^{\mu/kT} \Rightarrow f_j \equiv \frac{N_j}{g_j} \frac{1}{e^{(\varepsilon_j - \mu)/kT}}$$

COMPARISON OF THE DISTRIBUTIONS

Distribution functions for identical indistinguishable particles

$$\frac{N_j}{g_j} = \frac{1}{e^{(\varepsilon_j - \mu)/kT} + a} \qquad ☛ \qquad a = \begin{cases} +1 & \text{for FD statistics} \\ -1 & \text{for BE statistics} \\ 0 & \text{for MB statistics} \end{cases}$$



STATISTICAL THERMODYNAMICS OF IDEAL GAS

Consider ideal gas in a sufficiently large container

Levels of system are quantized so finely ☛ introduce density of states $\rho(\varepsilon)$

Number of particles in quantum states within energy interval $d\varepsilon$

# of particles in one state $f(\varepsilon)$ times # of states dn_ε in this energy interval

With $f(\varepsilon)$ given by (49)

$$dN_\varepsilon = f(\varepsilon) dn_\varepsilon = \frac{N}{Z} e^{-\beta\varepsilon} \rho(\epsilon) d\varepsilon$$

For finely quantized levels ☛ replace summation by integration

$$\sum_i \ldots \Rightarrow \int d\varepsilon \rho(\varepsilon) \ldots$$

Partition function ☛

$$Z = \int d\varepsilon \, \rho(\varepsilon) \, e^{-\beta\varepsilon}$$

MAXWELL SPEED DISTRIBUTION

For quantum particles in a rigid box

$$Z = \frac{V}{(2\pi)^2}\left(\frac{2m}{\hbar}\right)^{3/2}\int_0^\infty d\varepsilon\,\sqrt{\varepsilon}e^{-\beta\varepsilon} = \frac{V}{(2\pi)^2}\left(\frac{2m}{\hbar^2}\right)^{3/2}\frac{\sqrt{\pi}}{2\beta^{3/2}} = V\left(\frac{mk_\beta T}{2\pi\hbar^2}\right)^{3/2} \quad (51)$$

Using $\varepsilon = mv^2/2$ and $d\varepsilon = mvdv$

number of particles in speed interval dv ☛ $dN_v = N(v)dv = N\ f(v)\ dv$

$$f(v) = \frac{1}{Z}e^{-\beta\varepsilon}\rho(\varepsilon)\,mv = \frac{1}{V}\left(\frac{2\pi\hbar^2}{mk_BT}\right)^{3/2}\frac{V}{(2\pi)^2}\left(\frac{2m}{\hbar^2}\right)^{3/2}\sqrt{\frac{m}{2}}vmve^{-\beta\varepsilon}$$

$$= \left(\frac{m}{2\pi k_BT}\right)^{3/2}4\pi v^2\exp\left(-\frac{mv^2}{2k_BT}\right)$$

coincides with result from kinetic theory of gases

Plank's constant $\hbar$ ☛ link to quantum mechanics disappeared from final result

EQUATION OF STATE OF IDEAL GAS

Internal energy of ideal gas is its kinetic energy $U = N\bar{\varepsilon}$

$\bar{\varepsilon} = m\bar{v}^2/2$ being average kinetic energy of an atom

From kinetic theory ☛ $\bar{\varepsilon} = \dfrac{f}{2} k_B T$

$f = 3$ corresponding to three translational degrees of freedom

Same result obtained from (51) and $U = \sum_{i=1}^{n} \varepsilon_i N_i = \dfrac{N}{Z} \sum_{i=1}^{n} e^{-\beta \varepsilon_i} = -\dfrac{N}{Z}\dfrac{\partial Z}{\partial \beta}$

$$U = -N \frac{\partial \ln Z}{\partial \beta} = -N \frac{\partial}{\partial \beta} V \ln\left(\frac{m}{2\pi\hbar^2\beta}\right)^{3/2} = \frac{3}{2} N \frac{\partial}{\partial \beta} \ln \beta = \frac{3}{2} N \frac{1}{\beta} = \frac{3}{2} N k_B T$$

P is defined by thermodynamic formula ☛ $P = -\left(\dfrac{\partial F}{\partial V}\right)_T$

With help of (51)

$$P = N k_B T \frac{\partial \ln Z}{\partial V} = N k_B T \frac{\partial \ln V}{\partial V} = \frac{N k_B T}{V}$$

that amounts to equation of state of ideal gas $PV = N k_B T$