5.62 Physical Chemistry II
Spring 2008

<u>5.62 Lecture #8</u>: Boltzmann, Fermi-Dirac, and Bose–Einstein Statistics

<u>THE DIRECT APPROACH TO THE PROBLEM OF INDISTINGUISHABILITY</u>

We could have approached the problem of indistinguishability by treating particles as indistinguishable fermions or bosons at the outset. QM tells us

1. All particles are indistinguishable

2. All particles are either fermions or bosons. The odd/even symmetry of a particle's wavefunction with respect to exchange is determined by whether the particle is a fermion or boson.

FERMION — a particle which obeys Fermi-Dirac statistics;
many-particle wavefunction is antisymmetric (changes sign) *with respect to exchange of any pair of identical particles*: $P_{12}\psi = -\psi$

1/2 integer spin

e^{-}, proton, ^{3}He

Single state occupation number: $n_i = 0$ or $n_i = 1$, no other possibilities!

BOSON — a particle which obeys Bose-Einstein statistics;
many-particle wavefunction is symmetric (does not change sign) *with respect to exchange of any pair of identical particles*

^{4}He, H_2, photons integer spin

n_i = any number, without restriction

What kind of particle is ^{6}Li, ^{7}Li, D, D^{+}?

We are going to figure out how to write

$$\Omega(\{n_i\}) = \prod_{i=1}^{t} \frac{\omega(n_i, g_i)}{N!}$$

where we are considering level i with energy ε_t and degeneracy g_i. Previously we had considered $\Omega(\{n_i\})$ for non-degenerate states rather than g_i-fold degenerate ε_i levels.

Let us play with some simple examples before generalizing results for each type of system.

3 degenerate states: A, B, C (states could be x, y, z directions for particle in cube)
2 particles: 1, 2

A	B	C
1	2	
1		2
2	1	
2		1
	1	2
	2	1
1,2		
	1,2	
		1,2

If particles are distinguishable and there are no restrictions on occupancy, total # of distinguishable arrangements is 3^2. Note that this is different from the degeneracy of a particular set of occupation numbers for non-degenerate states, $\dfrac{N!}{\prod n_i!}$.

For each degenerate level occupied by particles, we have a factor:

particles

degeneracy of atomic state

$$\omega(n,g) = g^n$$

to correct for particle indistinguishability. We divide by N!

$$\Omega_B\left(\{n_i\}\right) = \frac{\prod_{i=1}^{t} \omega(n_i,g_i)}{N!} = \frac{\prod_{i=1}^{t} g_i^{n_i}}{N!}$$

For our case $\dfrac{3^2}{2!} = 4.5$ which is not an integer so $\dfrac{g^n}{n!}$ can be only an approximation to the correct total # of ways.

Now go to F–D system

occupation # is 0 or 1, indistinguishable particles, therefore $g \geq n$.

$\omega_{FD}(n,g) = \left[\dfrac{g!}{(g-n)!}\right]\dfrac{1}{n!}$

put excitation first in any of g states, 2nd in any of g–1, then divide by n! for indistinguishability of particles. Finally, divide by (g – n)! for indistinguishability of "holes".

$$\Omega_{FD}\left(\{n_i\}\right) = \frac{\prod_{i=1}^{t} \omega_{FD}(g_i, n_i)}{N!} = \frac{\prod_{i=1}^{t} \left[\dfrac{g_i!}{(g_i - n_i)!n!}\right]}{N!}$$

A	B	C
X	X	
X		X
	X	X

$g = 3$, $n = 2$

$\omega_{FD} = \dfrac{3!}{2!1!} = 3$

Now for B–E

what is the combinatorial factor?

n particles

g distinguishable states $\rightarrow$ g–1 indistinguishable partitions

arrange n indist. particles and g–1 indist. partitions in all possible orders

$$\omega_{BE}(N,g) = \frac{(n+g-1)!}{n!(g-1)!}$$

$$\Omega_{BE}\left(\{n_i\}\right) = \frac{\prod_{i=1}^{t} \omega_{BE}(n_i, g_i)}{N!} = \frac{\prod_{i=1}^{t} \dfrac{(n_i + g - 1)!}{n_i!(g-1)!}}{N!}$$

for our case $\dfrac{(2+3-1)!}{2!(3-1)!} = \dfrac{4!}{2!2!} = 6$

A	B	C
XX		
	XX	
		XX
X	X	
X		X
	X	X

for our example

$$\begin{array}{ccc} \omega_{FD} < & \omega_{B} < & \omega_{BE} \\ 3 & 4.5 & 6 \end{array}$$

always true — compare $\omega(n_i,g_i)$ factors in $\Omega(\{n_i\})$ term by term. This means that $\overline{n_i}$ for a degenerate level is always largest for BE and smallest for FD. Why?

Before starting the general, rigorously derivable result for $\overline{n_i}$ for BE, corrected Boltzmann, and FD, we need to derive a relationship between μ and q for corrected Boltzmann statistics.

$$A = -kT \ln Q = -kT \ln (q^N/N!) = -NkT \ln q + kT \ln N!$$

for large N, ln N! = N ln N – N. This is Stirling's approximation. Very, very useful.

$$A = -NkT\ln q + NkT\ln N - NkT$$

$$\mu \equiv \left(\frac{\partial A}{\partial N}\right)_{T,V} = -kT\ln q + kT\ln N + NkT(1/N) - kT$$

$$= -kT\ln q + kT\ln N$$

$$= -kT\ln(q/N)$$

$$-\frac{\mu}{kT} = \ln(q/N)$$

$$e^{-\mu/kT} = q/N$$

$$q = Ne^{-\mu/kT}$$ which is a very convenient form.

The probability of finding one particle out of N in level ε_i is

$$P_i = \frac{\overline{n_i}}{N} = \frac{e^{-\varepsilon_i/kT}}{q}$$ which are the standard definition and statisitical mechanical values of P_i

$$\overline{n_i} = Ne^{-\varepsilon_i/kT}/q$$

replace q

$$\overline{n_i} = Ne^{-\varepsilon_i/kT}/(Ne^{-\mu/kT}) = \frac{1}{e^{(\varepsilon_i-\mu)/kT}}$$

This is the corrected Boltzmann result for $\overline{n_i}$. Notice that when $\varepsilon_i < \mu$, $\overline{n_i} > 1$ which violates the assumption upon which the validity of corrected Boltzmann depends. Note also, that when $T \to 0$, the only occupied levels are those where $\varepsilon_i \le \mu$. When $\varepsilon_i > \mu$ and $T = 0$, $\overline{n_i} = 0$. Note further, from the derived T dependence of μ

$$\mu = -kT \ln (q/N)$$

$$\lim_{T\to 0} \mu = 0$$

Thus, as $T \to 0$, the only occupied level in $\varepsilon_i = 0$ which has occupancy $\overline{n_{\varepsilon=0}} = 1$.

It is clear that we need to replace corrected Boltzmann statistics by BE or FD as $T \to 0$ and whenever $\overline{n}_i^B$ becomes comparable to 1.

Assert (derived for Grand Canonical Ensemble, where μ, V, and T are held constant, pp. 431-439 of Hill)

$$\overline{n_i} = \frac{1}{e^{(\varepsilon_i-\mu)/kT} \pm 1} \qquad \begin{array}{l} +1 \text{ is FD} \\ -1 \text{ is BE} \\ \text{no 1 is B} \end{array}$$

This equation obeys the expectation

$$\overline{n}_i^{FD} < \overline{n}_i^{B} < \overline{n}_i^{BE}$$

In the limit of $T \to 0$

	$\underline{\varepsilon_i = \mu}$	$\underline{\varepsilon_i < \mu}$	$\underline{\varepsilon_i > \mu}$
$\overline{n}_i^{BE}$	$\to \infty$	< 0 (impossible)	0
$\overline{n}_i^{FD}$	$\to \frac{1}{2}$	1	0
$\overline{n}_i^{B}$	$\to 1$	∞ (illegal)	0

First, let's make sure "exact" result for $\overline{n_i}$ is correctly normalized to total number of particles.

$$N = F \sum_i \overline{n_i} = F \sum_i \frac{1}{e^{(\varepsilon_i-\mu)/kT} \pm 1}$$

normalization correction factor

so

$$F = \frac{N}{\sum_i \frac{1}{e^{(\varepsilon_i-\mu)/kT} \pm 1}} \qquad \text{normalization factor}$$

$$\overline{n}_i = F\overline{n}_i = \frac{N}{(e^{(\varepsilon_i-\mu)/kT} \pm 1)\sum_j \frac{1}{e^{(\varepsilon_j-\mu)/kT} \pm 1}}$$

normalized "exact" result

approximate result being checked for normalization

Now make the Boltzmann approximation $e^{(\varepsilon_j-\mu)/kT} \gg 1$ for all j

The factors of ±1 are small and can be neglected, thus:

$$\overline{n}_i = \frac{N}{e^{(\varepsilon_i-\mu)/kT}\sum_j e^{-(\varepsilon_j-\mu)/kT}} =$$

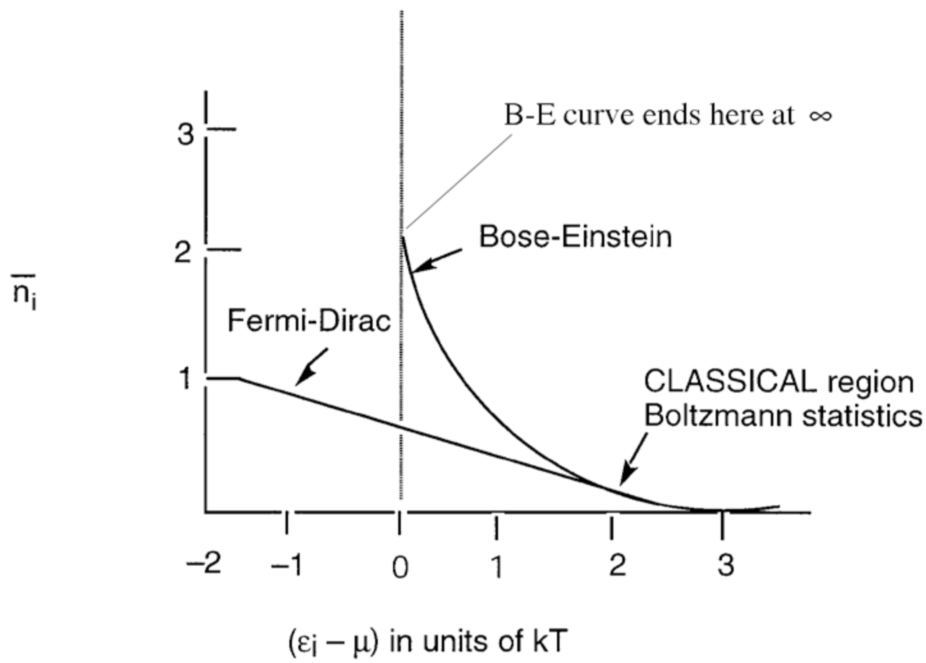
$$\overline{n}_i = \frac{Ne^{-\varepsilon_i/kT}}{\sum_j e^{-\varepsilon_j/kT}} = \frac{Ne^{-\varepsilon_i/kT}}{q}$$

CORRECTLY REDUCES TO BOLTZMANN STATISTICS RESULT!

PLOT the FD and BE distribution functions for $\overline{n}_i$. $\overline{n}_i$ vs. $\dfrac{\varepsilon_i - \mu}{kT}$

Note that:

* $\overline{n}_i$ cannot be larger than 1 for FD
* $\overline{n}_i$ goes to ∞ when $\varepsilon_i = \mu$ for BE
* when $\overline{n}_i \approx 1$, we are no longer allowed to use corrected Boltzmann.



For large $\varepsilon_i - \mu$ and consequently large $e^{(\varepsilon_i-\mu)/kT}$ or $\overline{n}_i << 1$,

$$\overline{n}_i^{FD} = \overline{n}_i^{BE}$$

and when these occupation numbers are equal

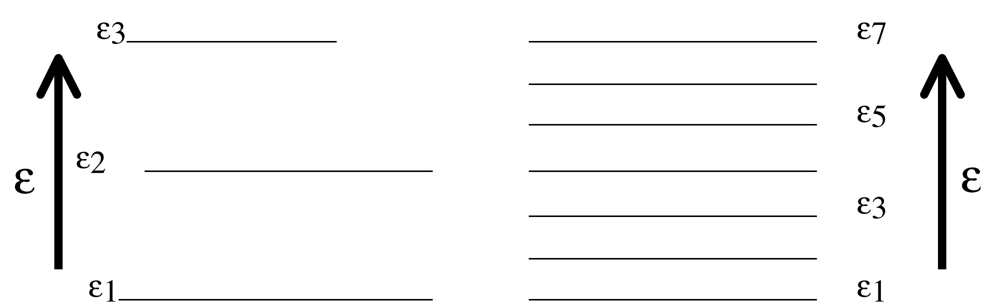
$$\overline{n_i} << 1 \ !$$

Most atoms and molecules at "ordinary" temperatures are in Boltzmann regime where $\overline{n_i} << 1$ or $q >> N$. In this case, there is no difference between FD and BE statistics. Doesn't matter if the molecule is a fermion or boson. So the Boltzmann statistics we have developed is valid over a wide range of molecules and conditions.

EXCEPTIONS: ^4He and H_2 are BOSONS.
Must be treated as such at T close to 0K.
^3He is FERMION.
Must be treated as such at T close to 0K.

Notice that the exceptions are lighter atoms and molecules at low T. That's because as you make particle less massive, the spacings in energy between the particle's states get larger, leading to fewer available states. If fewer states are available, $\overline{n_i}$ goes up, and eventually the difference between FD and BE statistics becomes discernible.

$$\varepsilon_i = \frac{h^2}{8ma^2}\left(n_x^2 + n_y^2 + n_z^2\right)$$



LIGHT PARTICLE
* $\overline{n_i}$ is larger
* may have to use FD or BE statistics

HEAVY PARTICLE
* $\overline{n_i}$ is smaller

At "normal" temperatures > ~20K, can treat ^3He, ^4He, H_2 with Boltzmann statistics.

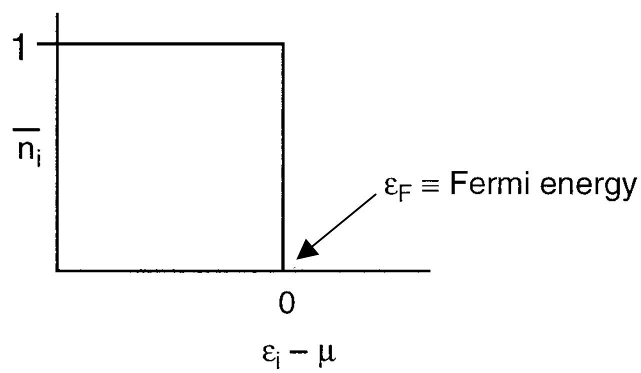
So temperature plays a role here too. We'll talk about this next time.

BUT ELECTRONS always have to be treated as FERMIONS for all "normal" temperatures (<3000K), because their $\overline{n_i}$'s $\simeq 1$.

> The valence electrons of the Au atoms which make up a gold crystal are delocalized throughout the crystal. These electrons can be thought of as an electron gas contained within the crystal. This is called a free electron model where the energy levels of electrons are particle-in-box energy levels. The average number of electrons in each electron state is given by the Fermi-Dirac distribution function

$$\boxed{\overline{n_i}} = \boxed{\frac{1}{e^{(\varepsilon_i - \mu)/kT} + 1}} \qquad \text{F.D.}$$

At T = 0

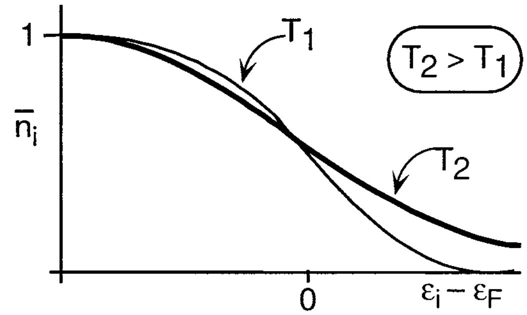


We fill each state with 1 e⁻ in order of increasing energy. The energy at which we run out of e⁻s is $\varepsilon_i = \mu$. In Solid State Physics language

$$\mu \equiv \varepsilon_F \quad \text{FERMI ENERGY}$$

which is the maximum energy that an e⁻ can have at T = 0.

AT T > 0K



Electrons move from occupied to unoccupied states as T is increased. Must move to unoccupied states because $\overline{n_i} > 1$ not allowed. This is the origin of conductivity in metals. [More on this in second half of course.]

Non-Lecture

Alternative Derivation of $\bar{n}_i$ for B-E and F-D Particles

Canonical p. f. $$Q = \sum_{\{n_i\}} \Omega(\{n_i\}) e^{-\beta n_i \varepsilon_i}$$ (this is actually a sum over sets of occupation numbers, $\{n_i\}$, *and* over states, i)

$$= \sum_{\{n_i\}} \prod_i \left[\omega(n_i) e^{-\beta n_i \varepsilon_i}\right]$$

$\omega(n_i)$ is the number of distinguishable ways of arranging n_i particles in the ε_i single-particle energy level.

The form of $\omega(n)$ depends on the particle statistics.

If it were possible to evaluate this sum, then we could determine $\bar{n}_i$ from

$$\bar{n}_i \equiv -kT\left(\frac{\partial \ln Q}{\partial \varepsilon_i}\right)_{V,T,N} = \frac{-kT}{Q}\frac{\partial Q}{\partial \varepsilon_i}$$

$$= -\frac{kT}{Q}\sum_{\{n_i\}}\left(\frac{-n_i}{kT}\right)\Omega(\{n_i\}) e^{-\beta n_i \varepsilon_i}$$

$$= \frac{\sum_{\{n_i\}} n_i \Omega(\{n_i\}) e^{-\beta n_i \varepsilon_i}}{Q} \equiv \bar{n}_i.$$

Now we will evaluate Q approximately by finding the single set of occupation numbers $\{n_i\}$ that gives the maximum term in the sum over occupation numbers that defines Q. The approximation is to set Q equal to the value of this maximum term in the sum. There remains a sum over states, *i*.

This approximation can only be valid if the maximum term in the sum is vastly larger than any term corresponding to a different set of occupation numbers.

This is a common and useful approximation in statistical mechanics.

Find the maximum term in the sum, call it Q_M and assume $Q_M \approx Q$

$$A = -kT \ln Q_M$$

$$-\beta A = \ln Q_M = \sum_i{}' \left\{\ln\left[\omega(n_i)\right] - \beta \varepsilon_i n_i\right\},$$

we have kept only the single set of occupation numbers that gives the maximum term in the sum that defines Q.

The prime on the $\sum_i'$ implies the constraint

$$\mathrm{N} = \sum_i n_i$$

Use Lagrange multipliers to impose this constraint so that the constrained sum can be replaced by an unconstrained sum,

$$-\beta A = \ln Q_M = \underbrace{\sum_i}_{\text{unconstrained sum}} \left\{ \ln\left[\omega(n_i)\right] - \beta\varepsilon_i n_i \right\} + \underset{\substack{\uparrow \\ \text{value to be chosen}}}{\lambda} \underbrace{\left(\sum_i n_i - N \right)}_{=0}$$

$$-\beta\left(\frac{\partial A}{\partial N}\right)_{V,T} = -\lambda$$

$$\text{but } \left(\frac{\partial A}{\partial N}\right)_{V,T} = \mu \qquad\qquad \text{Thus } \lambda = \beta\mu = \frac{\mu}{kT}.$$

Insert the derived specific value for λ,

$$-\beta A = \sum_i \left\{ \ln\left[\omega(n_i)\right] - \beta(\varepsilon_i - \mu) n_i \right\} - N\beta\mu\,,$$

rearrange

$$\mathrm{N}\beta\mu - \beta\mathrm{A} = \sum_{\mathrm{i}} \left\{ \ln\left[\omega(\mathrm{n_i}) - \beta\left(\varepsilon_{\mathrm{i}} - \mu\right) \mathrm{n_i} \right] \right\}$$

and use the thermodynamic identity

$$G = N\mu = A + pV$$

$$\beta(N\mu - A) = \beta pV = \ln Q + N\beta\mu = \sum_i \left\{ \ln\left[\omega(n_i)\right] - \beta(\varepsilon_i - \mu) n_i \right\}$$

Now we choose particular forms for $\omega(n_i)$ and insert them into the above equation for βpV. Note that we have not yet addressed the approximation of Q by Q_M.

A. **Corrected Boltzmann**

g_i is the degeneracy of the single-particle ε_i energy level, and n_i is the number of particles in the assembly in the ε_i energy level.

$$\omega_B = \frac{g^n}{n!}$$
$$\ln \omega_B = n \ln g - n \ln n + n$$
$$\beta pV = \sum_i \left\{ n_i \ln g_i - n_i \ln n_i + n_i - \beta(\varepsilon_i - \mu) n_i \right\}$$

to obtain the maximum term in this sum, we take a derivative wrt each n_i. For each n_i

$$\left(\frac{\partial}{\partial n_i}(\beta pV)\right)_{V,T,N} = \left\{ \ln(g_i) - \ln n_i - 1 + 1 - \beta(\varepsilon_i - \mu) \right\} = 0, \text{ thus}$$
$$n_i^B = g_i e^{-\beta\varepsilon_i} e^{\beta\mu}$$

(note $\dfrac{\partial^2(\beta pV)}{\partial n_i^2} = -(1/n_i) < 0$ which assures that the extremum is a maximum and not a minimum).

Since $q = \mathrm{N}e^{-\beta\mu}$, we get the standard corrected Boltzmann result when we replace $e^{\beta\mu}$ by N/q,

$$\frac{\overline{n}_i^B}{N} = \frac{g_i e^{-\beta\varepsilon_i}}{q},$$

moreover, when we replace the original sum over sets of $\{n_i\}$ that defines βpV by the specific set $\{n_i\}$ that gives the maximum term in the sum, we get

$$\beta pV = \sum_i \left\{ n_i \ln \frac{g_i}{n_i} + n_i - \beta(\varepsilon_i - \mu) n_i \right\}$$
$$\frac{g_i}{n_i} = e^{\beta(\varepsilon_i - \mu)}$$
$$n_i \ln(g_i/n_i) = n_i \beta(\varepsilon_i - \mu).$$

Thus

$$\beta pV = \sum_i n_i = N$$

which is the ideal gas law.

B. **Fermi-Dirac**

$$\omega_{FD}(g,n) = \frac{g!}{n!(g-n)!}$$

$$\beta pV = \sum_i \left\{\ln\left[\omega(n_i) - \beta(\varepsilon_i - \mu)n_i\right]\right\}$$

$$\beta pV = \sum_i \left\{g_i \ln g_i - g_i - n_i \ln n_i + n_i - (g_i - n_i)\ln(g_i - n_i) + (g_i - n_i) - \beta(\varepsilon_i - \mu)n_i\right\}$$

$$-g_i + n_i + (g_i - n_i) = 0$$

The extremum term in the sum over sets of $\{n_i\}$ is obtained from taking $\frac{\partial}{\mathrm{dn_i}}$ and setting result = 0.

$$\left(\frac{\partial(\beta pV)}{\partial n_i}\right)_{V,T,N} = \left\{\ln(g_i - n_i) - \ln n_i - \beta(\varepsilon_i - \mu)\right\} = 0 \quad \text{for all } i.$$

$$\ln\frac{g_i - n_i}{n_i} = \beta(\varepsilon_i - \mu)$$

$$\frac{g_i - n_i}{n_i} = \frac{g_i}{n_i} - 1 = e^{\beta(\varepsilon_i - \mu)}$$

$$\frac{g_i}{n_i} = e^{\beta(\varepsilon_i - \mu)} + 1$$

Thus

$$n_i^{FD} = g_i \frac{1}{e^{\beta(\varepsilon_i - \mu)} + 1},$$

replacing the sum in Q by its maximum term, Q_M

$$\beta pV = \sum_i \left\{g_i \ln g_i - n_i \ln n_i - g_i \ln(g_i - n_i) + n_i \ln(g_i - n_i) - \beta(\varepsilon_i - \mu)n_i\right\}$$

$$= \sum_i \left\{g_i \ln g_i - g_i \ln(g_i - n_i) + n_i \ln\frac{g_i - n_i}{n_i} - \beta(\varepsilon_i - \mu)n_i\right\}$$

but, for the term in the sum over sets of $\{n_i\}$ that has the maximum value

$$\ln\frac{g_i - n_i}{n_i} = \beta(\varepsilon_i - \mu)$$

and the last two terms in { } cancel. We obtain

$$\beta pV = -\sum_i g_i \ln \frac{g_i - n_i}{g_i} = -\sum_i g_i \ln\left(1 - \frac{n_i}{g_i}\right)$$
$$= -\sum_i g_i \ln\left(1 - \frac{1}{e^{\beta(\varepsilon_i - \mu)} + 1}\right)$$
$$= -\sum_i g_i \ln\left(\frac{e^{\beta(\varepsilon_i - \mu)} + 1 - 1}{e^{\beta(\varepsilon_i - \mu)} + 1}\right)$$
$$= \sum_i g_i \ln\left(\frac{e^{\beta(\varepsilon_i - \mu)} + 1}{e^{\beta(\varepsilon_i - \mu)}}\right) = \sum_i g_i \ln\left[1 + e^{\beta(\mu - \varepsilon_i)}\right]$$

which is *not* the ideal gas law. However, at high ε,

$$\ln\left[1 + e^{\beta(\mu - \varepsilon)}\right] \to e^{\beta(\mu - \varepsilon)}$$

because, for $x \ll 1$

$$\ln(1+x) = \ln 1 + \frac{1}{1+0} x + \ldots$$
$$\approx x$$

and, for $x = e^{\beta(\mu - \varepsilon)}$ when $\varepsilon \gg \mu$

$$e^{\beta(\mu - \varepsilon)} \ll 1 .$$

Thus

$$\beta pV = \sum_i g_i e^{\beta(\mu - \varepsilon_i)} = \sum_i g_i e^{\beta\mu} e^{-\beta\varepsilon_i}$$
$$e^{-\beta\mu} = (q/N)$$
$$\beta pV = \sum_i \frac{N g_i e^{-\beta\varepsilon_i}}{q} = N\frac{q}{q} = N$$

which is the ideal gas law!

C. **Bose-Einstein**

$$\omega_{BE}(n_i) = \frac{(g_i + n_i - 1)!}{n_i!(g_i - 1)!}$$

Thus

$$\ln \omega_{BE}(n_i) = \sum_i \left\{(g_i + n_i - 1)\ln(g_i + n_i - 1) - (g_i + n_i - 1) - n_i \ln n_i + n_i - (g_i - 1)\ln(g_i - 1) + g_i - 1\right\}$$
$$= \sum_i \left\{(g_i + n_i - 1)\ln(g_i + n_i - 1) - n_i \ln_i n_i - (g_i - 1)\ln(g_i - 1)\right\}$$

$$\beta pV = \ln Q + N\beta\mu = \sum_{\{n_i\}} \left\{\ln \omega_{BE}(n_i) - \beta(\varepsilon_i - \mu)n_i\right\}.$$

The set of occupation numbers that gives the largest contribution to βpV is obtained from

$$\left(\frac{\partial(\beta pV)}{\partial n_i}\right)_{V,T,N} = 0 = \ln\left(g_i + n_i - 1\right) + \frac{g_i + n_i - 1}{g_i + n_i - 1} - \ln n_i - \frac{n_i}{n_i} - \beta\left(\varepsilon_i - \mu\right)$$

thus

$$\ln\frac{g_i + n_i - 1}{n_i} = \beta\left(\varepsilon_i - \mu\right)$$

$$\frac{g_i - 1}{n_i} + 1 = e^{\beta(\varepsilon_i - \mu)}$$

$$n_i^{BE} = \left(g_i - 1\right)\frac{1}{e^{\beta(\varepsilon_i - \mu)} - 1}$$

Since $g_i \gg 1$, we obtain the usual result

$$n_i^{BE} = \frac{g_i}{e^{\beta(\varepsilon_i - \mu)} - 1}$$

and, when $\varepsilon_i = \mu$, the denominator vanishes and n_i^{BE} can be very large. This is the *Bose-Einstein* condensation. If $\varepsilon_i < \mu$, the nonsense result of a negative occupation number is obtained.

D. **Accuracy of the Maximum Term Approximation**
(see Hill, Appendix II, pp. 478-480).

$$Q \equiv \sum_{\{n_i\}}{}' \prod_{n_i} \left[\omega\left(n_i\right) e^{-\beta\varepsilon_i n_i}\right] \equiv \sum_{\{n_i\}} t\left(\{n_i\}\right)$$

where t($\{n_i\}$) is a typical term in the sum and $\sum'$ imposes the implicit constraint

$$\sum_i n_i = N \,.$$

Expand the value of the typical term t($\{n_i\}$) in the sum as a power series in deviations from the special set of occupation numbers $\{\hat{n}_i\}$ that give the maximum value of

$$\prod_{n_i} \left[\omega\left(n_i\right) e^{-\beta\varepsilon_i n_i}\right],$$

$$t_M = t\left(\{\hat{n}_i\}\right).$$

We have already used the requirement that $0 = \frac{\partial}{\partial n_i}\left[\omega\left(n_i\right) e^{-\beta\varepsilon_i n_i}\right]$ for all n_i to find the value of t_M and the set $\{\hat{n}_i\}$.

Thus

$$\ln t\left(\{n_i\}\right) = \ln t\left(\{\hat{n}_i\}\right) + \frac{1}{2}\sum_i \delta n_i^2 \frac{\partial^2 \ln\omega\left(\hat{n}_i\right)}{\partial n_i^2}\,.$$

The first nonzero term in the expansion involves the second derivatives because all of the first derivatives were required to be zero (condition for the maximum term)

$$\frac{\partial \ln t(\{\hat{n}_i\})}{\partial n_i} = 0$$

and the $e^{-\beta\varepsilon_i n_i}$ term is "used up" in the extremum condition. Thus the true value of Q is given in terms of the value of the maximum term in the sum over $\{n_i\}$ as

$$Q = Q_M \left(1 + \sum_{\{\delta n_i\}}' \exp\left[\frac{1}{2} \sum_i \delta n_i^2 \frac{\partial^2 \ln \omega(\hat{n}_i)}{\partial n_i^2} \right] + \ldots \right)$$

but, since we showed that the set $\{\hat{n}_i\}$ maximizes $t(\{n_i\})$, all of the second derivatives must be negative. This means the factor multiplying Q_M is $(1 + e^{-x})$ where $x > 0$ hence $Q \approx Q_M$. To make this argument stronger we need to compute these second derivatives and also realize that the exp[ ] contains many additive negative terms, thus $e^{-x} \to 0$.

The derivation of the second derivatives listed below is left as an exercise for you:

Statistics	$\frac{\partial^2 \ln \omega(\hat{n}_i)}{\partial n_i^2}$
Boltzmann	$-1/n_i$
Fermi-Dirac	$-\frac{g_i}{n_i(g_i - n_i)}$
Bose-Einstein	$-\frac{g_i - 1}{n_i(g_i + n_i - 1)}$