Quantum Statistics (Chapter 10 McQuarrie)

- half integral spin – Fermi-Dirac ⟶ electron, proton
- integral spin – Bose-Einstein ⟶ deuteron, photon

Composite particles

odd # of fermions – acts as fermion

even # of fermions – acts as a boson

$$\Xi(V,T,\lambda) = \prod_k \left(1 \pm \lambda e^{-\beta\varepsilon_k}\right)^{\pm 1}, \quad \lambda = e^{\beta\mu}$$

(1) $$N = \sum_k \frac{\lambda e^{-\beta\varepsilon_k}}{1 \pm \lambda e^{-\beta\varepsilon_k}}; \quad \overline{n}_k = \frac{\lambda e^{-\beta\varepsilon_k}}{1 \pm \lambda e^{-\beta\varepsilon_k}}$$

(2) $$E = \sum_k \frac{\lambda \varepsilon_k e^{-\beta\varepsilon_k}}{1 \pm \lambda e^{-\beta\varepsilon_k}}$$

(3) $$pV = \pm kT \sum_k \ell n\left(1 \pm \lambda e^{-\beta\varepsilon_k}\right)$$

upper – FD

lower - BE

solve (1) for λ, and substitute into (2) and (3)

In general, can't solve analytically for λ

If λ small, $\lambda = \frac{N}{q} \longrightarrow$ classical statistics (high T and low densities)

Even if particles are non-interacting, quantum effects cause deviations from $pV = NkT$

Weakly degenerate ideal Fermi-Dirac gas

$$N = \sum_k \frac{\lambda e^{-\beta\varepsilon_k}}{1+\lambda e^{-\beta\varepsilon_k}} \qquad pV = kT\sum_k \ell n\left(1+\lambda e^{-\beta\varepsilon_k}\right)$$

$$\varepsilon_k = \frac{h^2}{8mV^{2/3}}\left(n_x^2+n_y^2+n_z^2\right), \qquad n_x, n_y, n_z = 1, 2, \ldots$$

Counting states for translational problem

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

degeneracy = # ways $\frac{8ma^2\varepsilon}{h^2}$ can be written as $n_x^2 + n_y^2 + n_z^2$

Take sphere of radius $\sqrt{\frac{8ma^2\varepsilon}{h^2}} = R$

$$n_x^2 + n_y^2 + n_z^2 = \frac{8ma^2\varepsilon}{h^2} = R^2$$

for large *R* treat ε, *R* as continuous

states with energy $\leq \varepsilon$

$$\Phi = \frac{1}{8}\frac{4\pi R^3}{3} = \frac{\pi}{6}\left(\frac{8ma^2\varepsilon}{h^2}\right)^{3/2}$$

between $\varepsilon + \varepsilon\Delta\varepsilon$, such that $\Delta\varepsilon/\varepsilon << 1$

$$\omega = \Phi(\varepsilon + \Delta\varepsilon) - \Phi(\varepsilon)$$

$$\frac{\pi}{6}\left(\frac{8ma^2}{h^2}\right)^{3/2}\left[(\varepsilon + \Delta\varepsilon)^{3/2} - \varepsilon^{3/2}\right]$$

$$= \frac{\pi}{4}\left(\frac{8ma^2}{h^2}\right)^{3/2}\sqrt{\varepsilon}\Delta\varepsilon + \ldots$$

If $\varepsilon = \dfrac{3kT}{2}$ *, T = 300° K, m = 10^{-22} g, a = 10 cm, and* $\Delta\varepsilon = 0.01\varepsilon$

$$\omega \sim 10^{28}$$

for *N* particle system, the degeneracy is much larger: $\omega \sim 10^{10^{23}}$

$$\omega = 2\pi\left(\frac{2m}{h^2}\right)^{3/2} V\sqrt{\varepsilon}\Delta\varepsilon$$

$$\sum \rightarrow 2\pi\left(\frac{2m}{h^2}\right)^{3/2} V\int\sqrt{\varepsilon}\,d\varepsilon$$

$$N = 2\pi \left(\frac{2m}{h^2} \right)^{3/2} V \int_0^\infty \frac{\lambda \sqrt{\varepsilon} e^{-\beta\varepsilon} d\varepsilon}{1 + \lambda e^{-\beta\varepsilon}}$$

$$pV = 2\pi kT \left(\frac{2m}{h^2} \right)^{3/2} V \int_0^\infty \varepsilon^{1/2} \ell n \left(1 + \lambda e^{-\beta\varepsilon} \right) d\varepsilon$$

using the density of states from pages 10-11

Expand in powers of λ and integrate

(A) $$\rho = \frac{N}{V} = \frac{1}{\Lambda^3} \sum_{\ell=1}^{\infty} \frac{(-1)^{\ell+1} \lambda^{\ell}}{\ell^{3/2}} = \frac{1}{\Lambda^3} \left[\frac{\lambda}{1} - \frac{\lambda^2}{2^{3/2}} + \ldots \right]$$

(B) $$\frac{p}{kT} = \frac{1}{\Lambda^3} \sum_{\ell=1} \frac{(-1)^{\ell+1} \lambda^{\ell}}{\ell^{5/2}} = \frac{1}{\Lambda^3} \left[\lambda - \frac{\lambda^2}{2^{5/2}} + \ldots \right]$$

solve $\lambda = \lambda(\rho)$ using **(A)**

plug into (B) to get $\frac{p}{kT}$ as a function of ρ

Write $\lambda = a_0 + a_1\rho + a_2\rho^2 + \ldots$

$$\rho = \frac{1}{\Lambda^3}\left[\left(a_0 + a_1\rho + a_2\rho^2 + \ldots\right) + \frac{\left(a_0 + a_1\rho + a_2\rho^2 + \ldots\right)^2}{2^{3/2}} + \frac{\left(a_0 + a_1\rho + a_2\rho^2 + \ldots\right)^3}{3^{3/2}}\right]$$

$$\rho = \frac{1}{\Lambda^3}\left[\left(a_0 + \frac{a_0^2}{2^{3/2}} + \ldots\right) + \left(a_1 + \frac{2a_0a_1}{2^{3/2}} + \frac{3a_0a_1}{3^{3/2}} + \ldots\right)\rho + \left(a_2 + \ldots\right)\rho^2 + \ldots\right]$$

$$\Rightarrow a_0 = 0$$

$$\Rightarrow a_1 = \Lambda^3$$

$$\Rightarrow a_2 - \frac{a_1^2}{2^{3/2}} = 0$$

$$\Rightarrow \lambda = \rho\Lambda^3 + \frac{\left(\rho\Lambda^3\right)^2}{2^{3/2}} + \left(\frac{1}{4} - \frac{1}{3^{3/2}}\right)\left(\rho\Lambda^3\right)^3 + \ldots$$

$$\lambda = a_1\rho + a_2\rho^2 + a_3\rho^3 + \ldots$$

$$= \Lambda^3\rho + \frac{\Lambda^6}{2^{3/2}}\rho^2 + \ldots$$

$$\frac{p}{kT}=\frac{1}{\Lambda^3}\left[\frac{\lambda}{1}-\frac{\lambda^2}{2^{5/2}}+\frac{\lambda^3}{3^{5/2}}-\ldots\right]$$

$$\frac{p}{kT}=\frac{1}{\Lambda^3}\left[\frac{\left(a_1\rho+a_2\rho^2+\ldots\right)}{1}-\frac{\left(a_1\rho+a_2\rho^2+\ldots\right)^2}{2^{5/2}}+\ldots\right]$$

$$\frac{p}{kT}=\frac{1}{\Lambda^3}\left[\frac{\Lambda^3\rho}{1}+\left(a_2-\frac{a_1^2}{2^{5/2}}\right)\rho^2\Lambda^6+\ldots\right]$$

$$\frac{p}{kT}=\rho+\frac{\Lambda^3}{2^{5/2}}\rho^2+\left(\frac{1}{8}-\frac{2}{3^{5/2}}\right)\Lambda^6\rho^3\ldots$$

$$+\frac{\left(a_1\rho+\ldots\right)^3}{3^{5/2}}$$

$$\frac{a_1^2}{2^{3/2}}-\frac{a_1^2}{2^{5/2}}=\left(\frac{1}{2^{3/2}}-\frac{1}{2^{5/2}}\right)\Lambda^6$$

$$=\frac{1}{\sqrt{2}}\left(\frac{1}{2}-\frac{1}{4}\right)\Lambda^6=\frac{1}{4\sqrt{2}}\Lambda^6$$

$$\frac{p}{kT}=\frac{1}{\Lambda^3}\left[\Lambda^3\rho+\frac{\Lambda^6}{2^{3/2}}\right]$$

$$=\rho+B_2\rho^2+B_3\rho^3+\ldots$$

↑ 2nd virial coeff (B_2)

↑ 3rd virial coeff (B_3)

Virial coefficients reflect deviations away from ideality

B_2 is +, thus increases pressure beyond that for an ideal classical gas

Λ = thermal de Broglie wavelength

quantum effects < as de Broglie λ <

Actually it is $\dfrac{\Lambda^3}{V}$ that is a measure of quantum effects

$$E = \frac{3}{2}\frac{VkT}{\Lambda^3}\sum_{\ell=1}\frac{(-1)^{\ell+1}\lambda^{\ell}}{\ell^{5/2}}$$

$$= \frac{3}{2}NkT\left(1+\frac{\Lambda^3}{2^{5/2}}\rho+\ldots\right)$$

get expansion for μ from $\lambda = e^{\mu/kT}$
and S from $G = \mu N = E - TS + pV$

Of course, above approach only valid if quantum corrections are small

Now consider the strongly degenerate Fermi-Dirac gas

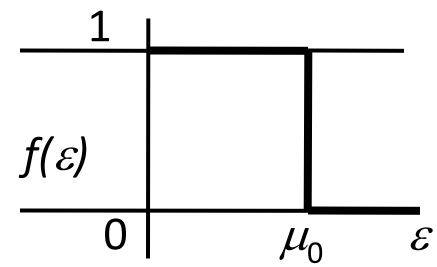
A model for the electrons in a metal

$$\bar{n}_K = \frac{\lambda e^{-\beta\varepsilon_k}}{1+\lambda e^{-\beta\varepsilon_k}} = \frac{1}{1+e^{\beta(\varepsilon_k-\mu)}}$$

since ε is essentially continuous

$$f(\varepsilon) = \frac{1}{1+e^{\beta(\varepsilon-\mu)}} =$$ prob. a state is occupied

$T = 0$, $\mu_0 = \mu$:
- states with $\varepsilon < \mu_0$ are occupied
- states with $\varepsilon > \mu_0$ are unoccupied



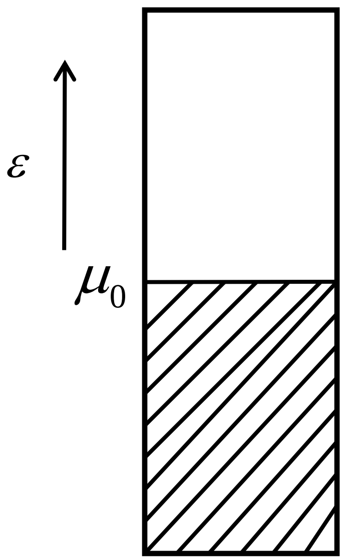
from 1-35

$$\omega(\varepsilon)d\varepsilon = 4\pi\left(\frac{2m}{h^2}\right)^{3/2} V\sqrt{\varepsilon}d\varepsilon$$

(includes factor of 2 for spin)

$$N = 4\pi\left(\frac{2m}{h^2}\right)^{3/2} V\int_0^{\mu_0}\sqrt{\varepsilon}d\varepsilon = \#\text{ valence } e^-$$

$$= \frac{8\pi}{3}\left(\frac{2m}{h^2}\right)^{3/2} V\mu_0^{3/2} \longrightarrow \mu_0 = \frac{h^2}{2m}\left(\frac{3}{8\pi}\right)^{2/3}\left(\frac{N}{V}\right)^{2/3}$$



at *T = 0*, the levels are double occupied up to μ_0

a finite *T*, the boundary is smeared out
i.e., some electrons are excited leaving "holes"

Even at room *T*

$$f(\varepsilon) = 1 \qquad \varepsilon < \mu_0$$

$$f(\varepsilon) = 0 \qquad \varepsilon > \mu_0$$

is a good approximation

$\mu_0 / k = T_F = \text{ Fermi } T,$ typically a few thousand degrees

$$E_0 = 4\pi\left(\frac{2m}{h^2}\right)^{3/2} V\int_0^{\mu_0} \varepsilon^{3/2} d\varepsilon = \frac{3}{5}N\mu_0 \quad \Big| \quad T = 0\ K$$

ZPE of FD gas

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only a very small fraction of the e^- are excited, so contribution to heat capacity is ~ 0

equipartition theorem would lead us to expect $\frac{3}{2}k$ for each electron

$$p = 4\pi kT\left(\frac{2m}{h^2}\right)^{3/2} \int_0^{\mu_0} \sqrt{\varepsilon}\,\ell n\left(1 + e^{\beta(\mu_0 - \varepsilon)}\right) d\varepsilon$$

ignore the "1"

$$p_0 = 4\pi\left(\frac{2m}{h^2}\right)\int_0^{\mu_0} \varepsilon^{1/2}\left(\mu_0 - \varepsilon\right) d\varepsilon$$

$$= \frac{2}{5}N\frac{\mu_0}{V}$$

⟵ zero-point pressure on the order of (10^6 atm)

$S_0 = 0$ only one way to occupy levels at $T = 0\ K$

It can be show that

$$\frac{\mu}{\mu_0} = 1 - \frac{\pi^2}{12}\eta^2 + \ldots, \qquad \eta = \frac{1}{\beta\mu_0}$$

$\mu \sim \mu_0$ for temperatures for which a metal is solid

$$E = E_0\left(\frac{\mu}{\mu_0}\right)^5\left[1 + \frac{5}{8}\pi^2\eta^2 + \ldots\right]$$

Note at T =0 K, $\mu = \mu_o$

$$C_v = \frac{\pi^2 NkT}{2\mu_0 / k} = \frac{\pi^2}{2} Nk\left(\frac{T}{T_f}\right)$$

~ *10^{-4} T cal/deg-mol*

weakly degenerate ideal Bose-Einstein gas

$$N = \sum \frac{\lambda e^{-\beta\varepsilon_k}}{1-\lambda e^{-\beta\varepsilon_k}}$$

$$pV = -kT\prod_k \ell n\left(1-\lambda e^{-\beta\varepsilon_k}\right)$$

$0 \le \lambda < e^{\beta\varepsilon_0}$, otherwise get 0 in denominator

$$N = \frac{\lambda e^{-\beta\varepsilon_0}}{1-\lambda e^{-\beta\varepsilon_0}} + \sum_{k\neq 0} \frac{\lambda e^{-\beta\varepsilon_k}}{1-\lambda e^{-\beta\varepsilon_k}}$$

redefine ε_0 to be *zero*

$$\rho = \frac{N}{V} = \frac{\lambda}{V(1-\lambda)} + 2\pi\left(\frac{2m}{h^2}\right)^{3/2} \int_{\varepsilon>0}^{\infty} \frac{\lambda \varepsilon^{1/2} e^{-\beta\varepsilon}}{1-\lambda e^{-\beta\varepsilon}} d\varepsilon, \qquad (0 \le \lambda < 1)$$

$$\frac{p}{kT} = -\frac{1}{V}\ell n(1-\lambda) - 2\pi\left(\frac{2m}{h^2}\right)^{3/2}\int_{\varepsilon>\varepsilon_0}^{\infty}\sqrt{\varepsilon}\,\ell n\left(1-\lambda e^{-\beta\varepsilon}\right)d\varepsilon$$

if λ *<< 1* can ignore *1/V* terms

$$\rho = \frac{1}{\Lambda^3} g_{3/2}(\lambda)$$

$$\frac{p}{kT} = \frac{1}{\Lambda^3} g_{5/2}(\lambda)$$

$$g_n = \sum_{\ell=1}^{\infty}\frac{\lambda^\ell}{\ell^n}$$

$$\frac{p}{\rho kT} = 1 - \frac{\Lambda^3}{2^{5/2}}\rho + \ldots$$

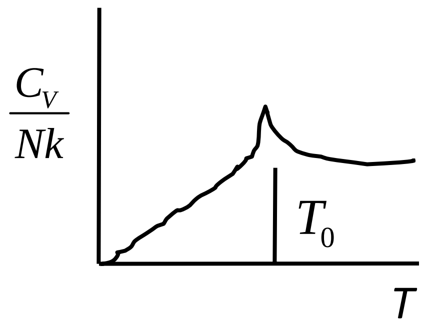
effective interaction between ideal bosons is attractive

$$E = \frac{3}{2}NkT\left(1 - \frac{\Lambda^3}{2^{5/2}}\rho + \ldots\right)$$

Strongly degenerate ideal Bose-Einstein gas

$T < T_0$ condensation into ground state

Behavior seen for *He-4*



From Wikepedia: A **Bose–Einstein condensate (BEC)** is a state of matter of a dilute gas of weakly interacting bosons confined in an external potential and cooled to T near to absolute zero. Under such conditions, a large fraction of the bosons occupy the lowest quantum state of the external potential, and quantum effects become apparent on a macroscopic scale. This state of matter was predicted by Bose and Einstein in 1924–25.

The first such condensate was produced by Cornell and Wieman in 1995 at the Univ. of Colorado NIST-JILA lab, using a gas of Rb atoms cooled to 170 (nK) [2]. Cornell, Wieman, and Ketterle (MIT) received the 2001 Nobel Prize in Physics.

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Ideal gas of photons

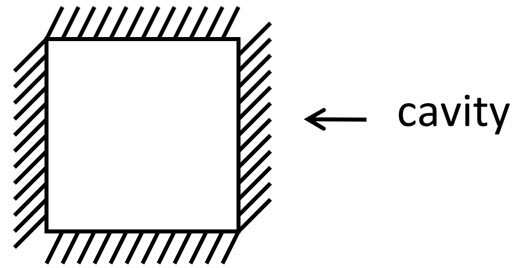
photons

mass = 0

ang mom $\hbar$

cavity emits/absorbs photons

N not fixed



Assume harmonic electromagnetic waves

$$E(x,t) = \sin\frac{2\pi}{\lambda}(x - ct) = \sin(kx - \omega t)$$

$$\varepsilon = h\upsilon = \hbar\omega; \quad p = h/\lambda = \hbar k$$

Consider black-body radiation to be due to standing waves

$$\phi(x,t) = 2\sin kx\cos\omega t$$

Fix at 0,L $\rightarrow$ k = nπ/L

$\varepsilon = \hbar c k$

$k^2 = (\pi/L)^2(n_x^2 + n_y^2 + n_z^2)$

$$E = \sum_k n_k \varepsilon_k$$

$$Q = \prod_k \left(\sum_n e^{-\beta \varepsilon_k n}\right) = \prod_k \frac{1}{(1 - e^{-\beta \varepsilon_k})}$$

$$E = \frac{\pi^2 V (kT)^4}{15(\hbar c)^3}$$

Can be used to derive the Stephan-Boltzmann law

Can also show that the chemical potential = 0 (follows from the fact that the number of particles is not conserved)

So could have used the Bose-Einstein formulas with $\lambda = 1$

Density matrices

All the expressions described above were derived assume there are no interactions between particles

$$Q = \sum_j e^{-\beta E_j}$$

$$\bar{M} = \frac{1}{Q}\sum_j M_j e^{-\beta E_j}, M_j = q.m.\text{ expectation value of operator } \hat{M}$$

$$H\psi_j = E_j \psi_j$$

$$e^{-\beta H}\psi_j = e^{-\beta E_j}\psi_j$$

$$Q = \sum_j e^{-\beta E_j} = \sum_j \langle \psi_j | e^{-\beta H} | \psi_j \rangle$$

$$Q = Tr(e^{-\beta H})$$

The trace is independent of the basis

$$\varphi_j = \sum_n a_{jn} \psi_n$$

Q is the same when evaluated over the φ_j

$$\bar{M} = \frac{Tr(\hat{M} e^{-\beta H})}{Tr(e^{-\beta H})}$$

$$\rho = \frac{e^{-\beta H}}{Tr(e^{-\beta H})}$$

$$\bar{M} = Tr(\hat{M}\rho)$$

$$H = \frac{-\hbar^2}{2m} \sum_l \nabla_l^2 + U(r_1, \ldots, r_N)$$

$$u(p_1, \ldots, r_N) = e^{\frac{i}{\hbar}\sum p_k \bullet r_k} \text{ = e.f. of momentum operator}$$

$$\varphi_j(r_1, \ldots r_N) = \int A_j(p_1, \ldots, p_N) e^{\frac{i}{\hbar}\sum p_k \bullet r_k} dp_1, \ldots, dp_N$$

$$A_j(p_1, \ldots, p_N) = \frac{1}{(2\pi\hbar)^{3N}} \int \varphi_j(r_1, \ldots r_N) e^{-\frac{i}{\hbar}\sum p_k \bullet r_k} dr_1, \ldots dr_N$$

Inverse Fourier transform

$$Q = \frac{1}{h^{3N}} \int \varphi_j * (r_1, \ldots r_N) \varphi_j (r_1', \ldots r_N') e^{-\frac{i}{\hbar}\sum p_k \bullet r_k'} e^{-\beta H} e^{\frac{i}{\hbar}\sum p_k \bullet r_k}$$

$$* dp_1, \ldots, dp_N dr_1, \ldots dr_N dr_1', \ldots dr_N'$$

$$Q = \frac{1}{h^{3N}} \int \; e^{-\frac{i}{\hbar}\sum p_k \bullet r_k'} e^{-\beta H} e^{\frac{i}{\hbar}\sum p_k \bullet r_k} \; p_1, \ldots dr_N$$

Now adopt a strategy due to Kirkwood

$$e^{-\beta H^{QM}} e^{\frac{i}{\hbar}\sum p_k \bullet r_k} = e^{-\beta H^{Cl}} e^{\frac{i}{\hbar}\sum p_k \bullet r_k} w(p_1, \ldots r_N, \beta) = F(p_1, \ldots r_N, \beta)$$

$$Q = \frac{1}{h^{3N}} \int e^{-\beta H^{Cl}} w(p_1, \ldots r_N, \beta) \, p_1, \ldots dr_N$$

$$\frac{\partial F}{\partial \beta} = -H^{QM} F$$

$$w = \sum_l \hbar^l w_l$$

$$w_0 = 1$$

$$w_2 = -\frac{1}{2m}\left\{\frac{\beta^2}{2}\nabla^2 U - \frac{\beta^3}{3}\left[(\nabla U)^2 + \frac{1}{m}(p \bullet \nabla)^2 U\right] + \frac{p^4}{2m}(p \bullet \nabla U)^2\right\}$$

Note we have not included the symmetry of the wavefunction which is why the N! is missing.

Contains the quantum corrections

It is easier to work with this diff.eq.

There is a w_1 term but it does not contribute to Q