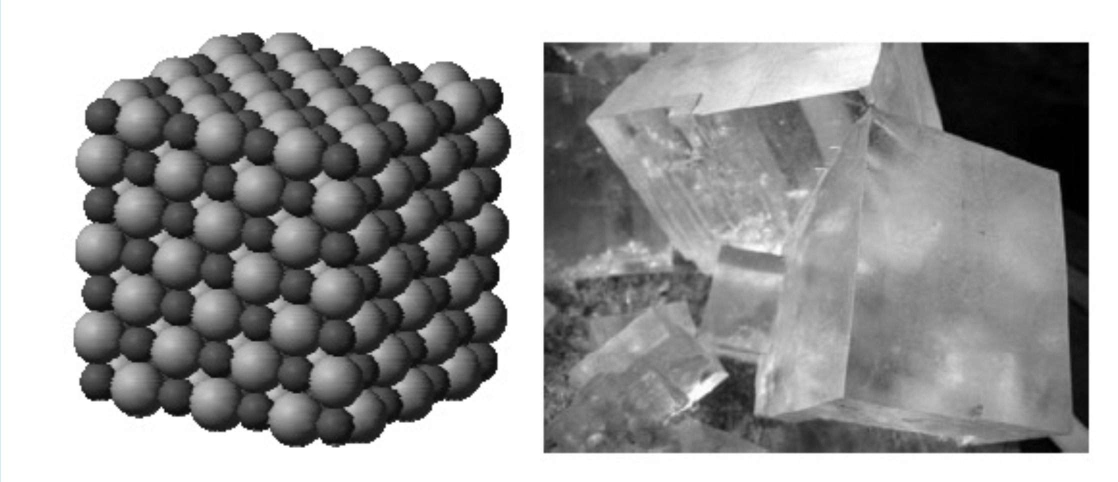
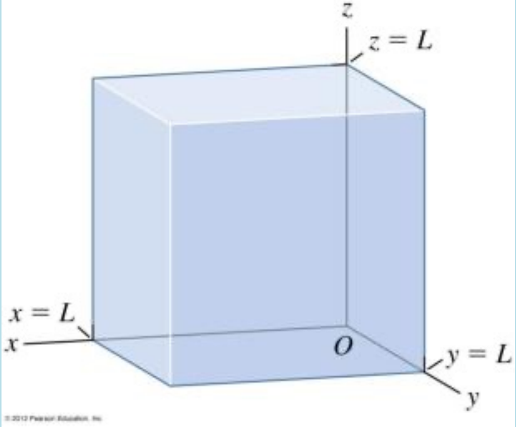
現在我們開始面對三維空間的固體。



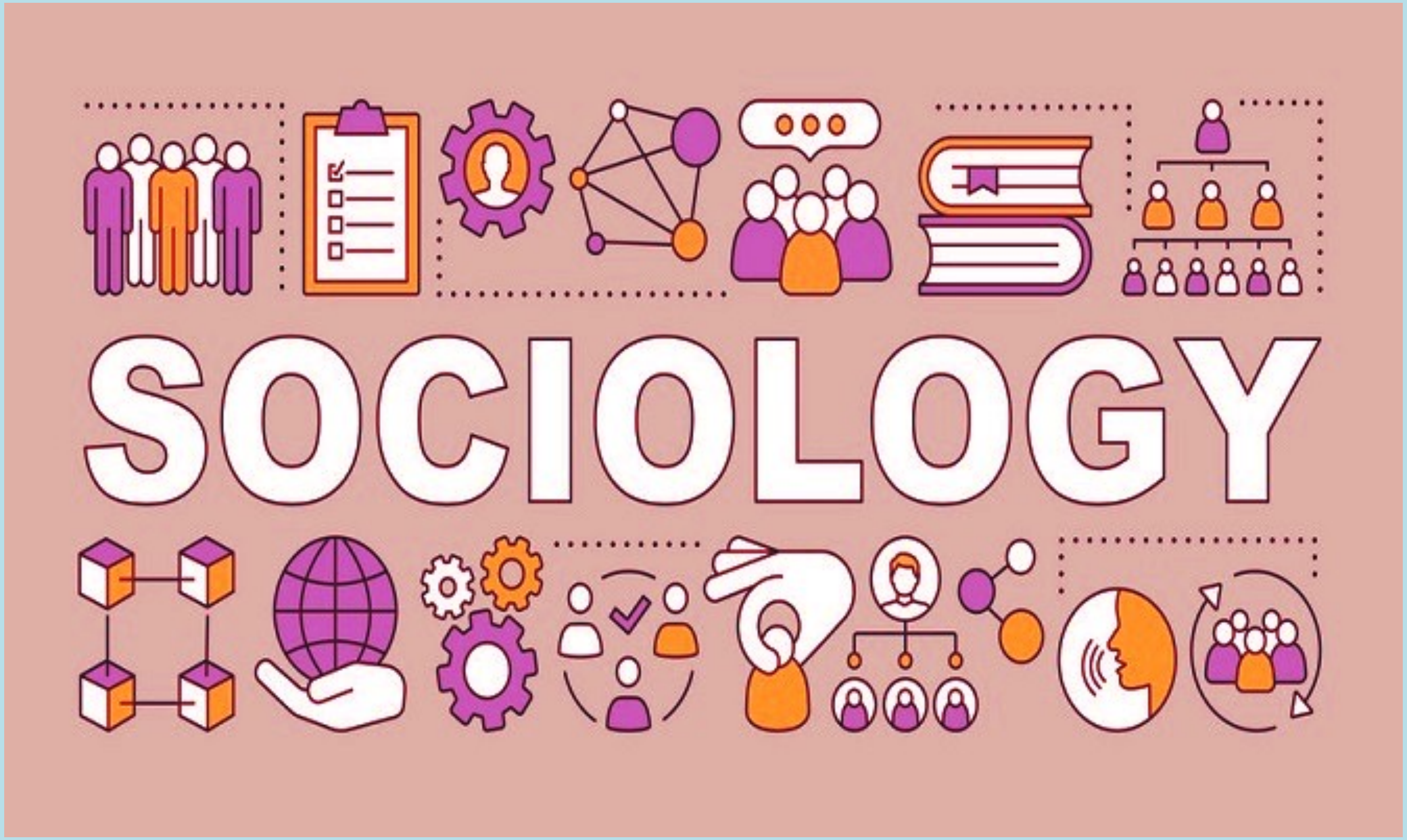
但避免同時面對兩個問題，我們將忽略晶格原子核的週期性位能。

因此將把固體看成自由空間，電子即自由電子。

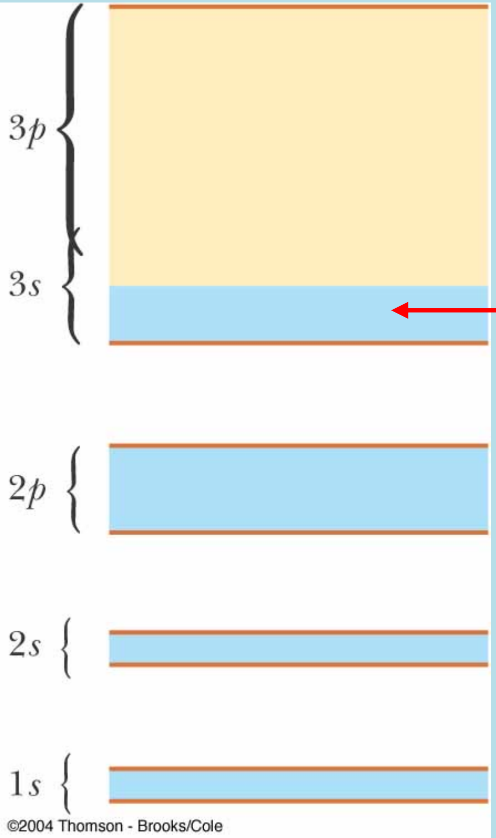


電子的社會學

Identical Particles 全同粒子



新的量子效應！彼此沒有交互作用的電子，其實會彼此影響。



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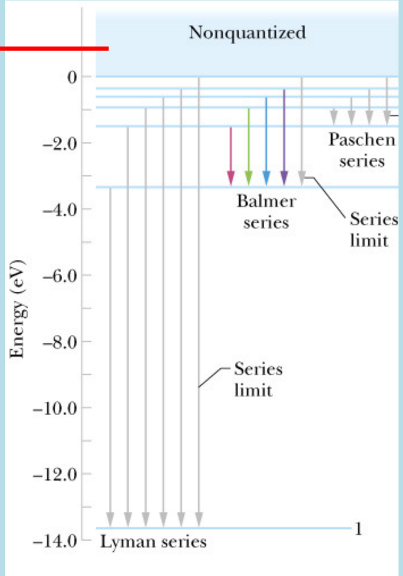


在未填滿的能帶內的電子能態，感覺就像原子能態中的連續能量自由態！

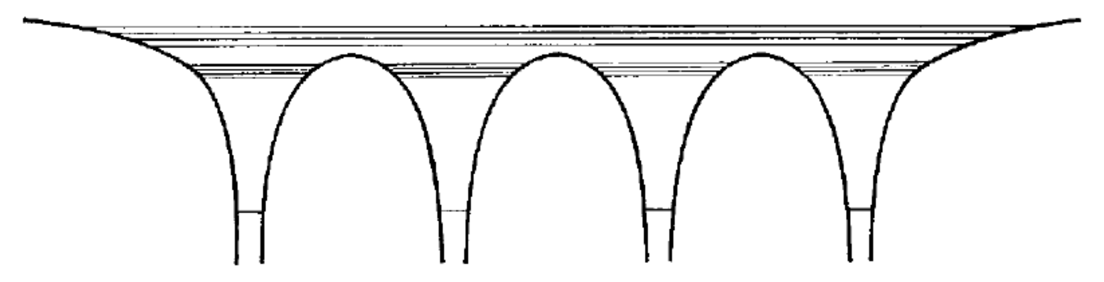
這些電子在固體內完全自由移動。彷彿沒有原子核存在一般。

因為固體對電子無比廣大，我們也可以暫時忽略電子彼此交互作用。

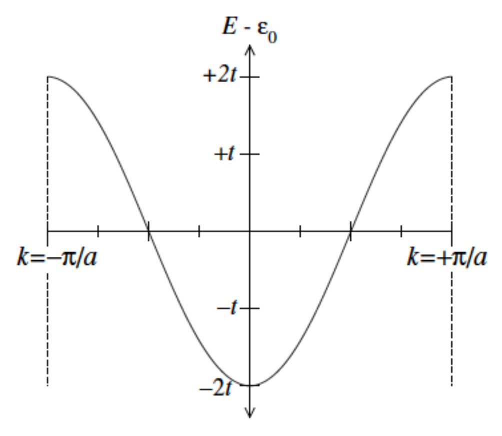
但彼此沒有作用的電子，其實會彼此影響。

Tight Binding Model

這些電子定態原來屬於私人，現在卻是公共財產！



計算發現：每一角波數k對應一定態，能量本徵值與k的關係如下圖：



在接近底部處，$E \sim E(0) + ta^2k^2$ 如同一自由電子，

對於這些底部電子，原子核的位能似乎不存在。

以沒有位能的定態，來描述三維導電固體中的電子，

三度空間Free Electron Model、Non-Interacting Electron Gas、(Sommerfeld Model)

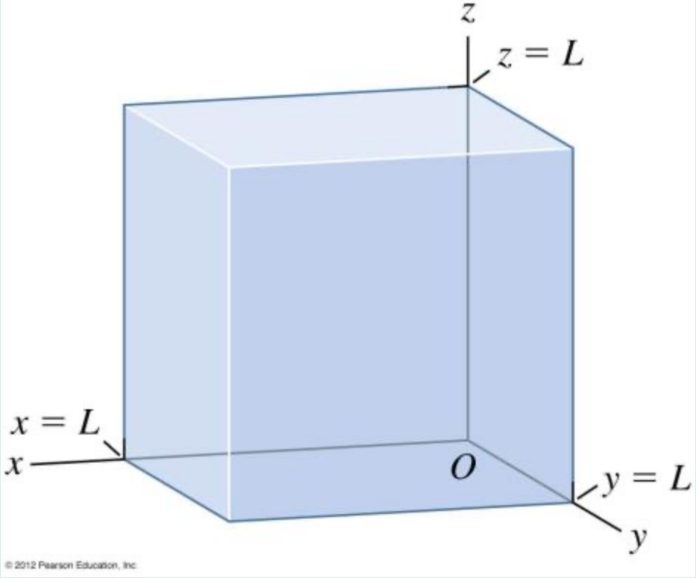
$$H = \frac{p^2}{2m}$$

能量本徵態的定態方程式：

$$H\psi_E(\vec{r}) = \frac{p^2}{2m}\psi_E(\vec{r}) = E\psi_E(\vec{r})$$

$$p^2 = -\hbar^2\left[\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right] = -\hbar^2\nabla^2$$

$$H\psi_E(\vec{r}) = -\frac{\hbar^2}{2m}\nabla^2\psi_E(\vec{r}) = E\psi_E(\vec{r})$$



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沒有位能。但的確有邊界。將固體想像為邊界無法透過的箱子。

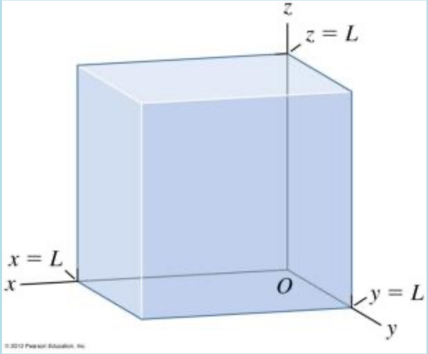
電子彼此無交互作用，求定態時單顆電子可分開處理，所以可以稱為理想氣體。

假設空間長度都是L，箱壁上波函數必須是零(或者滿足週期性條件)！

$$-\frac{\hbar^2}{2m}\left(\frac{\partial^2\psi_E}{\partial x^2}+\frac{\partial^2\psi_E}{\partial y^2}+\frac{\partial^2\psi_E}{\partial z^2}\right)=-\frac{\hbar^2}{2m}\nabla^2\psi_E=E\psi_E$$

三個座標分別獨立，可將定態波函數分解為三個變數個別函數的乘積：

$$\psi(x,y,z)=u(x)\cdot v(y)\cdot w(z)$$



代入定態方程式後，再除以ψ：

$$-\frac{\hbar^2}{2m}\left[\frac{1}{u}\frac{d^2u}{dx^2}(x)\right]-\frac{\hbar^2}{2m}\left[\frac{1}{v}\frac{d^2v}{dy^2}(y)\right]-\frac{\hbar^2}{2m}\left[\frac{1}{w}\frac{d^2w}{dz^2}(z)\right]=E$$

括號內分別只是x,y,z的函數，相加後為常數的唯一可能：

括號內都是常數，訂為E_1,E_2,E_3。

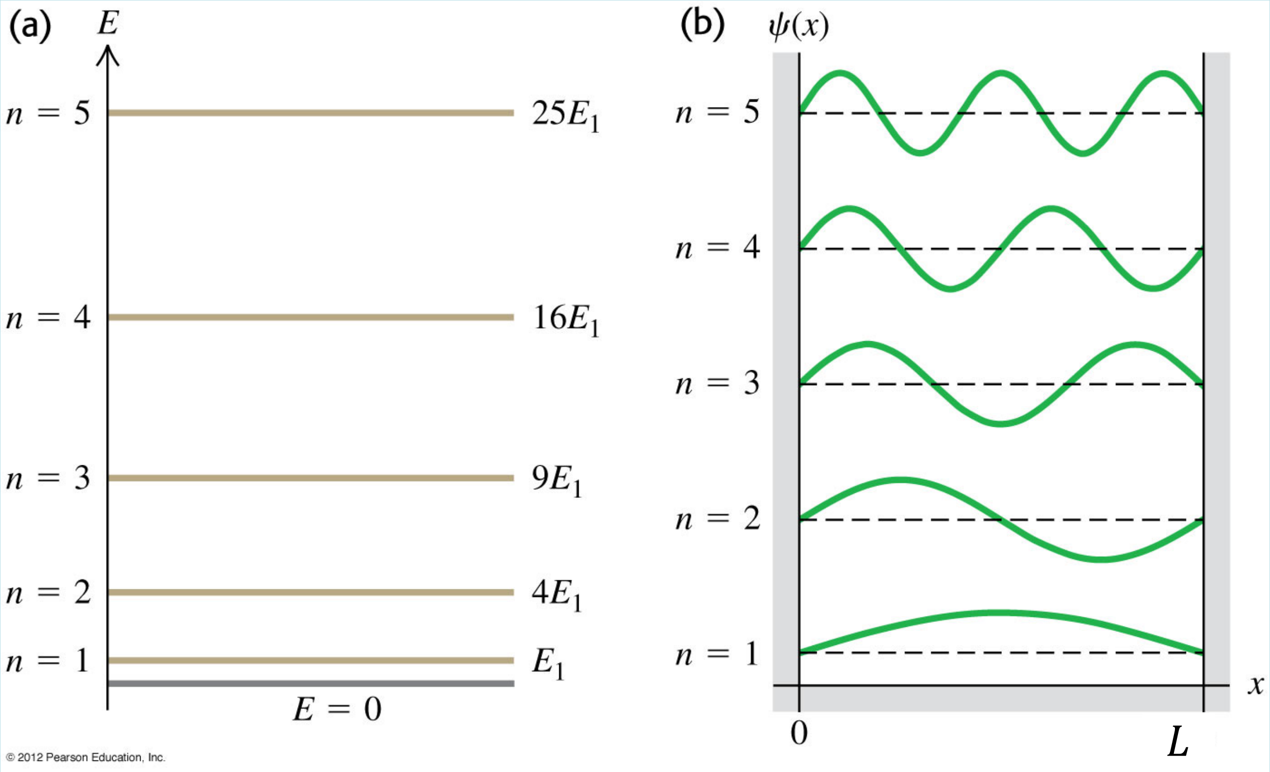
$$-\frac{\hbar^2}{2m}\frac{d^2u}{dx^2}=E_1u$$

$$-\frac{\hbar^2}{2m}\frac{d^2v}{dy^2}=E_2v$$

$$-\frac{\hbar^2}{2m}\frac{d^2w}{dz^2}=E_3w$$

$$E_1+E_2+E_3=E$$

三維Box簡化為三個一維Box！



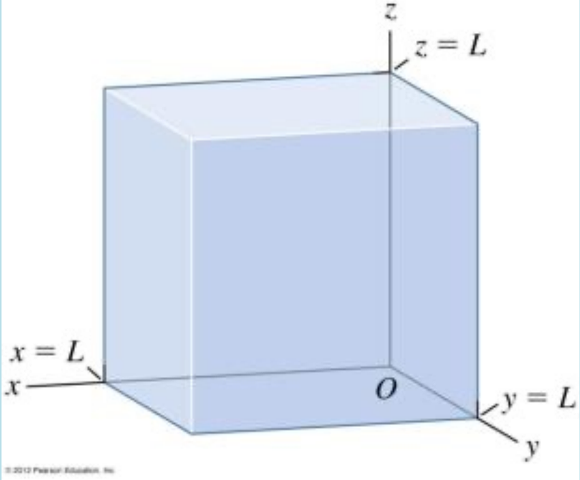
一維Box的定態以角波數k_n標定：

$$u_n = \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi}{L}x\right)$$

$$k_n = \frac{n\pi}{L}$$

能量等於：

$$E_n = \frac{\hbar^2\pi^2}{2mL^2}n^2$$



三維Box簡化為三個一維Box！

每一個方向個有一個角波數，因此各有一量子數n_x, n_y, n_z。

一組(n_x, n_y, n_z)對應一個定態！

$$u = \sqrt{\frac{2}{L}} \sin\left(\frac{n_x \pi}{L} x\right)$$

$$v = \sqrt{\frac{2}{L}} \sin\left(\frac{n_y \pi}{L} y\right)$$

$$w = \sqrt{\frac{2}{L}} \sin\left(\frac{n_z \pi}{L} z\right)$$

$$E_1 = \frac{\hbar^2 \pi^2}{2mL^2} n_x^2$$

$$E_2 = \frac{\hbar^2 \pi^2}{2mL^2} n_y^2$$

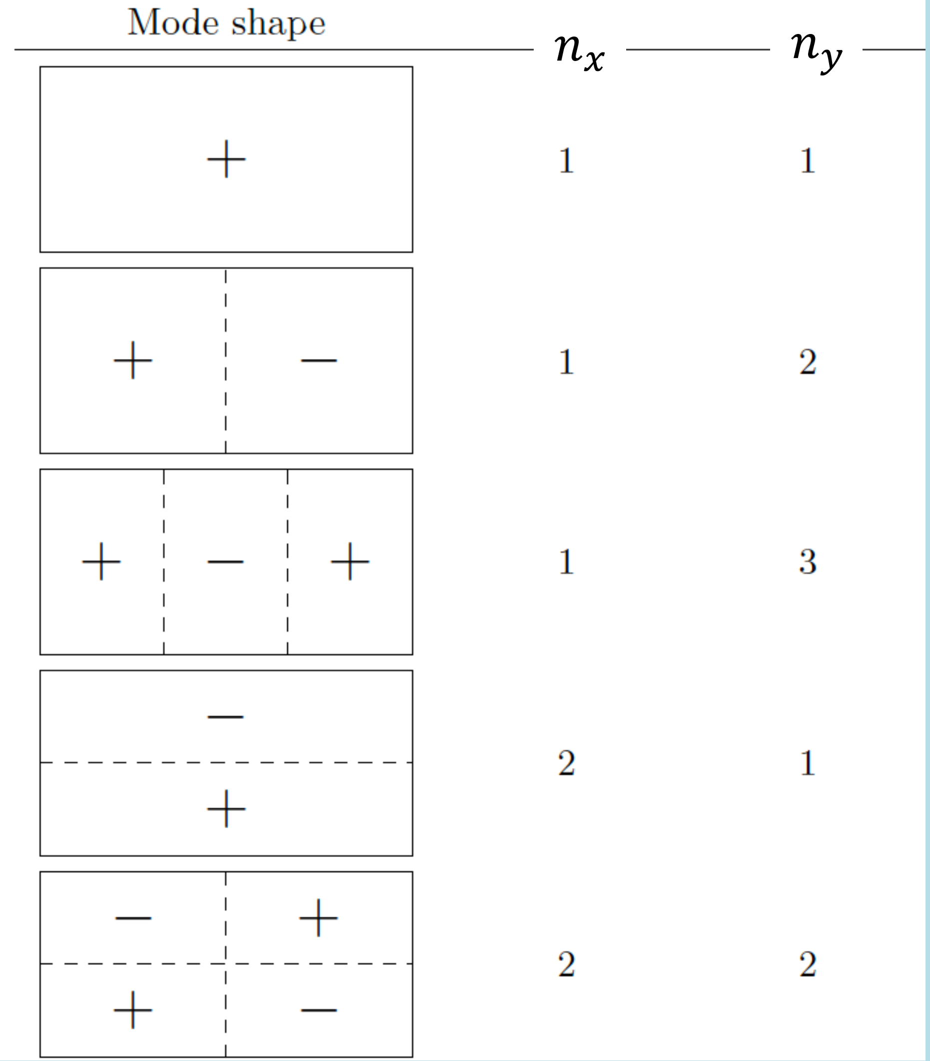
$$E_3 = \frac{\hbar^2 \pi^2}{2mL^2} n_z^2$$

(n_x, n_y, n_z)定態的能量：

$$E = \frac{\hbar^2 \pi^2}{2mL^2} \left(n_x^2 + n_y^2 + n_z^2\right)$$

$$\psi(x, y, z) = \left(\frac{2}{L}\right)^{\frac{3}{2}} \sin\left(\frac{n_x \pi}{L} x\right) \sin\left(\frac{n_y \pi}{L} y\right) \sin\left(\frac{n_z \pi}{L} z\right)$$

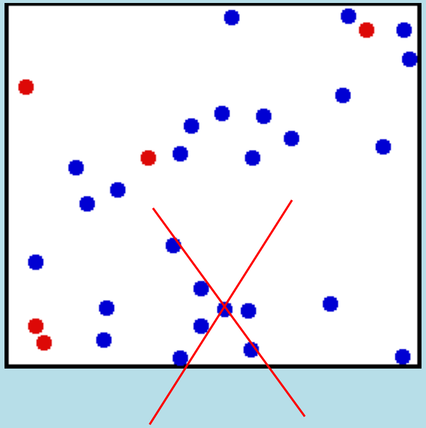
三維箱子內單一電子的定態之波函數。



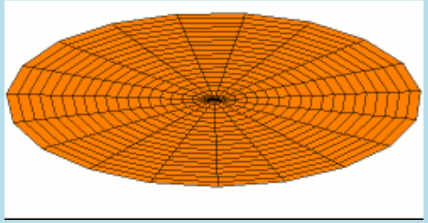
Mode shape	n_x	n_y
+	1	1
+ −	1	2
+ − +	1	3
− +	2	1
− + + −	2	2

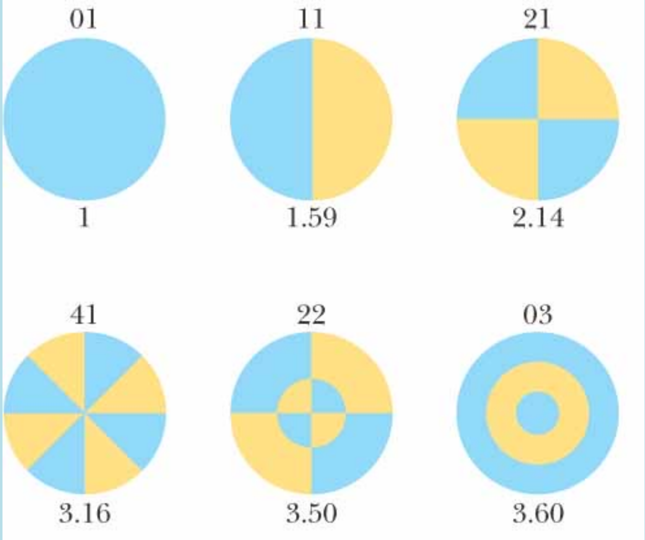
$n_{x,y,z}$就是各方向節點數目。

$$\left(\frac{2}{L}\right)^{\frac{3}{2}} \sin\left(\frac{n_x\pi}{L}x\right) \sin\left(\frac{n_y\pi}{L}y\right) \sin\left(\frac{n_z\pi}{L}z\right)$$

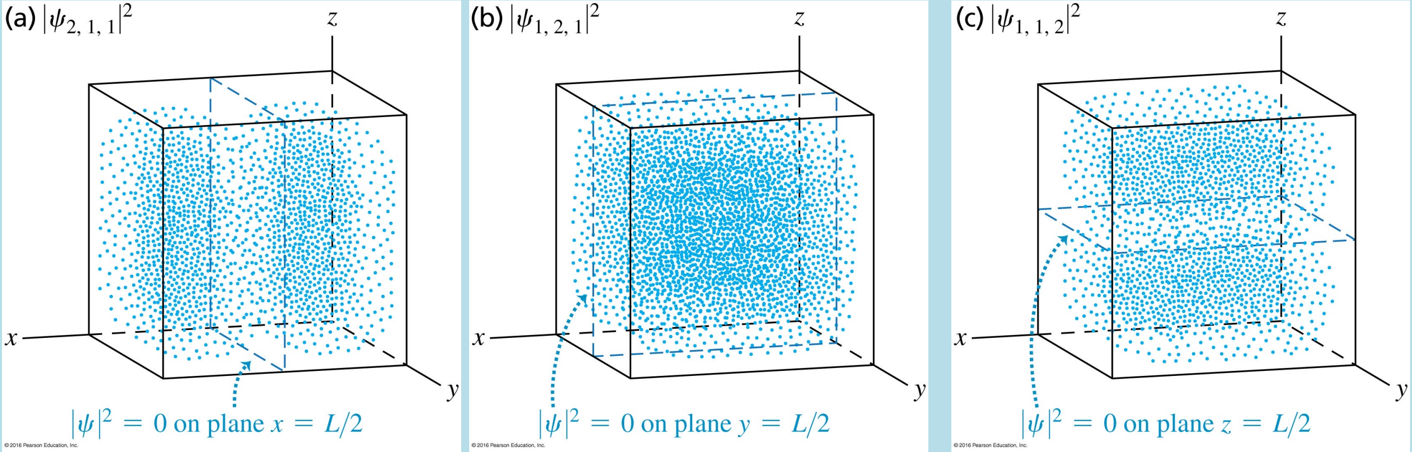


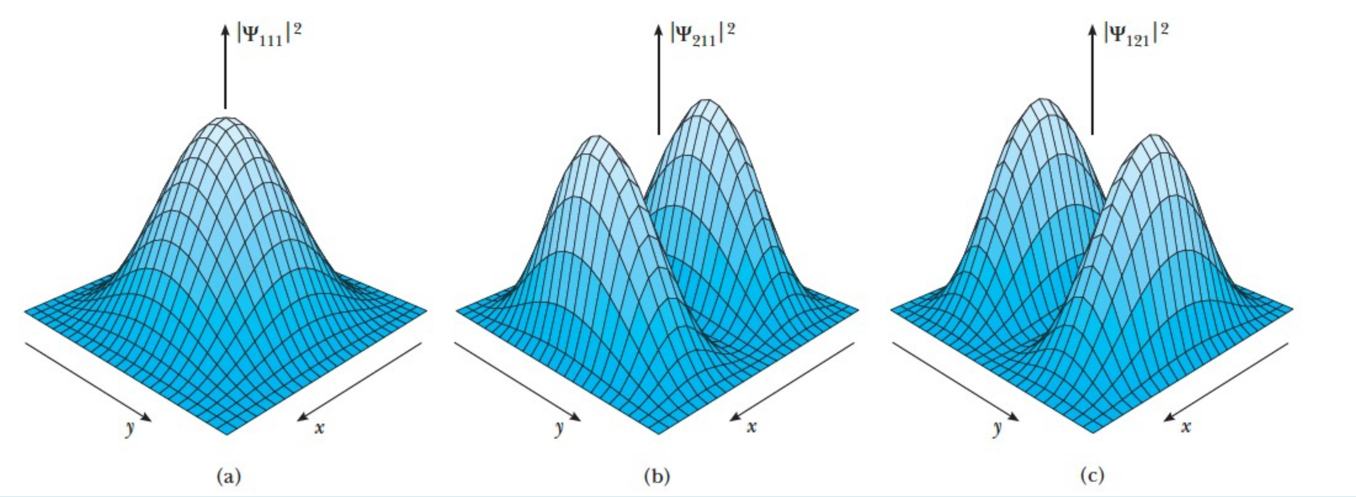
自由電子氣比較像駐波！





各定態機率密度：

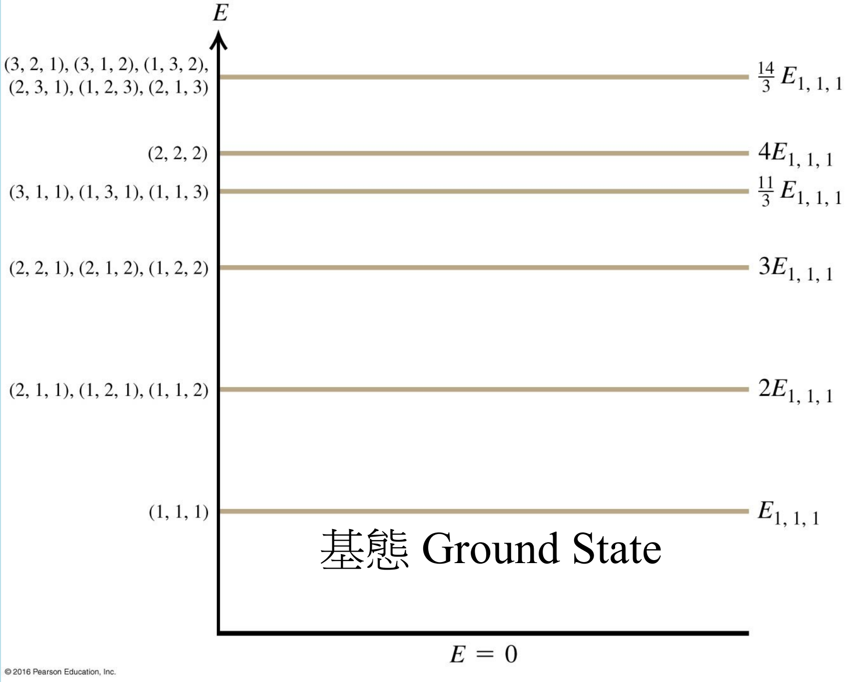

(a) $|\psi_{2,1,1}|^2$
x
y
z
$|\psi|^2 = 0$ on plane $x = L/2$
(b) $|\psi_{1,2,1}|^2$
x
y
z
$|\psi|^2 = 0$ on plane $y = L/2$
(c) $|\psi_{1,1,2}|^2$
x
y
z
$|\psi|^2 = 0$ on plane $z = L/2$


$|\Psi_{111}|^2$
y
x
$|\Psi_{211}|^2$
y
x
$|\Psi_{121}|^2$
y
x

(a) (b) (c)

(n_x, n_y, n_z)單一電子定態的能量，可如原子能階作圖：

$$E = \frac{\hbar^2\pi^2}{2mL^2}\left(n_x^2 + n_y^2 + n_z^2\right)$$



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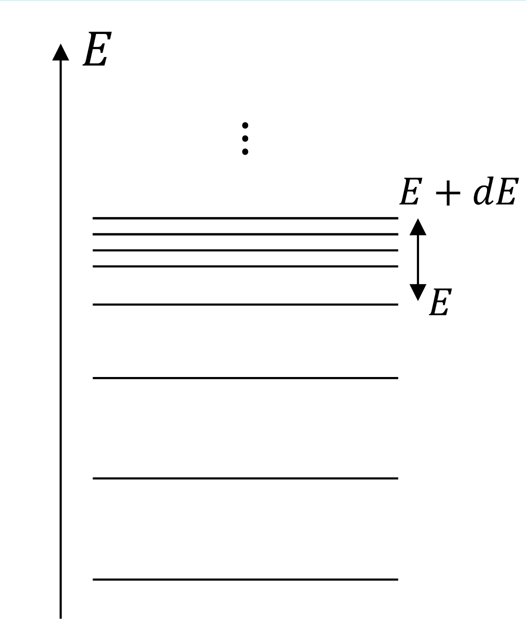
$$E_{2,1,1} = 6\frac{\hbar^2\pi^2}{2mL^2}$$

$$E_{1,1,1} = 3\frac{\hbar^2\pi^2}{2mL^2}$$



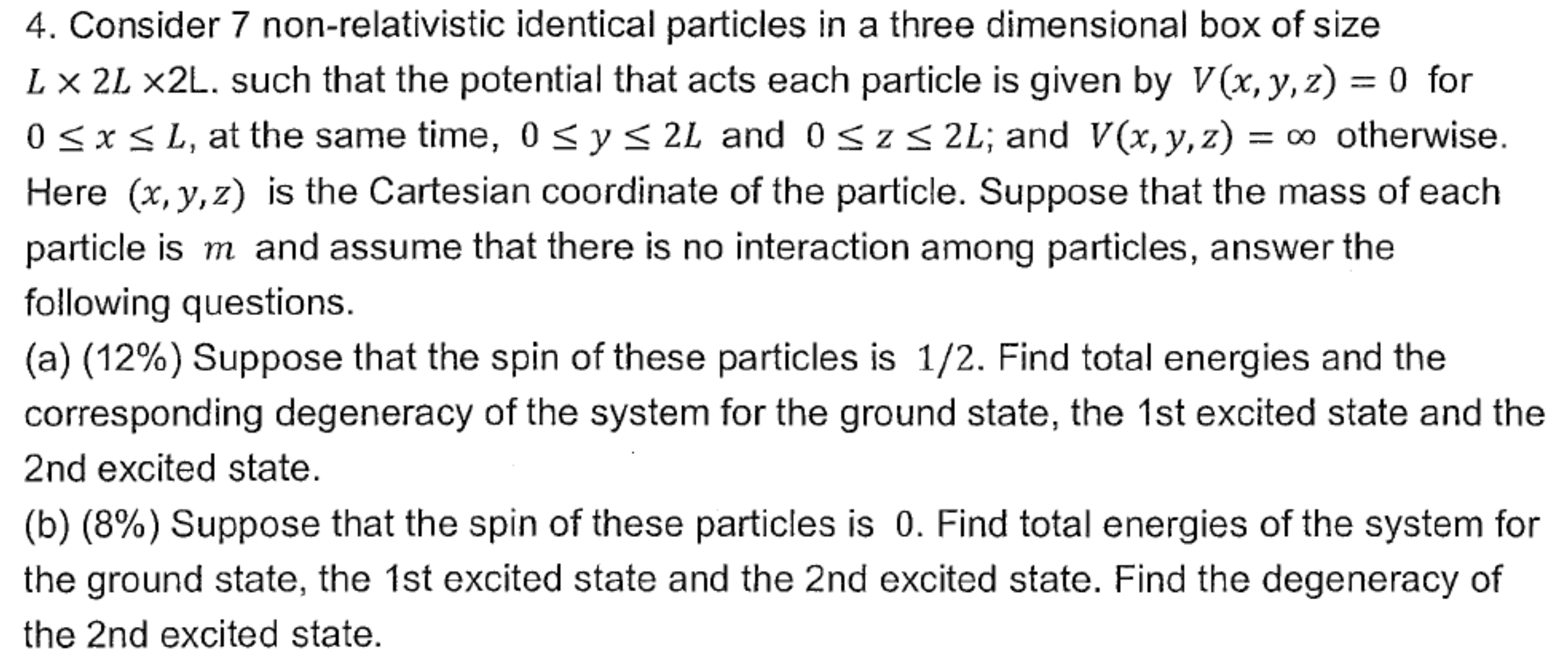
以能量為軸，定態的分布並不均勻！

與原子能階不同的是，電子氣的能階要放入數量龐大的電子。

當量子數越來越大時，能態的分佈趨近連續，但還是不均勻而有疏密之分！

可以定義上圖中電子狀態數目隨能量E的分布密度：density of states $g(E)$。

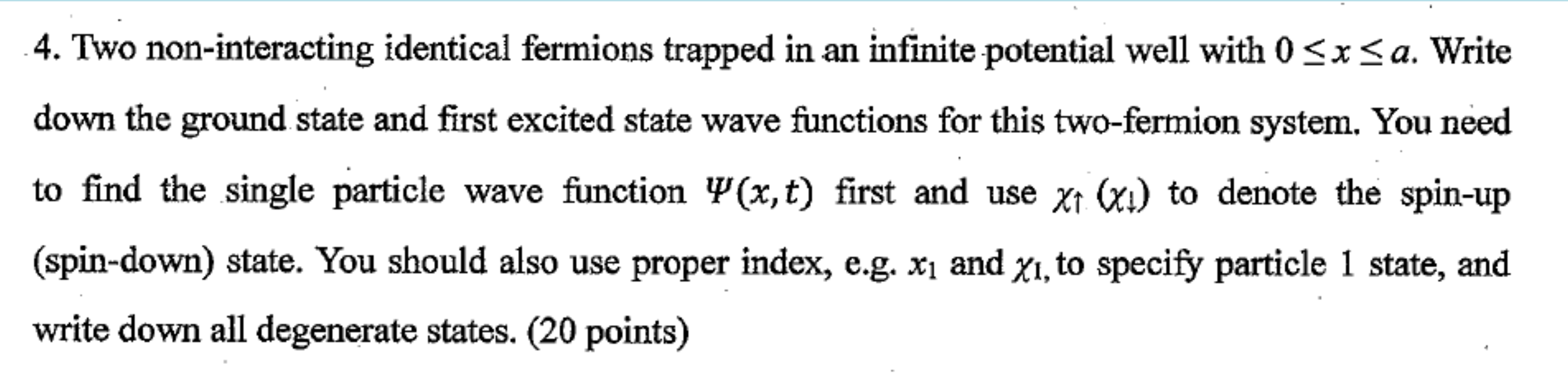
即能量介在E與$E + dE$之間的電子狀態數：$g(E) \cdot dE$



4. Consider 7 non-relativistic identical particles in a three dimensional box of size $L \times 2L \times 2L$. such that the potential that acts each particle is given by $V(x, y, z) = 0$ for $0 \leq x \leq L$, at the same time, $0 \leq y \leq 2L$ and $0 \leq z \leq 2L$; and $V(x, y, z) = \infty$ otherwise. Here (x, y, z) is the Cartesian coordinate of the particle. Suppose that the mass of each particle is m and assume that there is no interaction among particles, answer the following questions.

(a) (12%) Suppose that the spin of these particles is $1/2$. Find total energies and the corresponding degeneracy of the system for the ground state, the 1st excited state and the 2nd excited state.

(b) (8%) Suppose that the spin of these particles is 0. Find total energies of the system for the ground state, the 1st excited state and the 2nd excited state. Find the degeneracy of the 2nd excited state.



4. Two non-interacting identical fermions trapped in an infinite potential well with $0 \leq x \leq a$. Write down the ground state and first excited state wave functions for this two-fermion system. You need to find the single particle wave function $\Psi(x,t)$ first and use $\chi_\uparrow$ ($\chi_\downarrow$) to denote the spin-up (spin-down) state. You should also use proper index, e.g. x_1 and χ_1, to specify particle 1 state, and write down all degenerate states. (20 points)

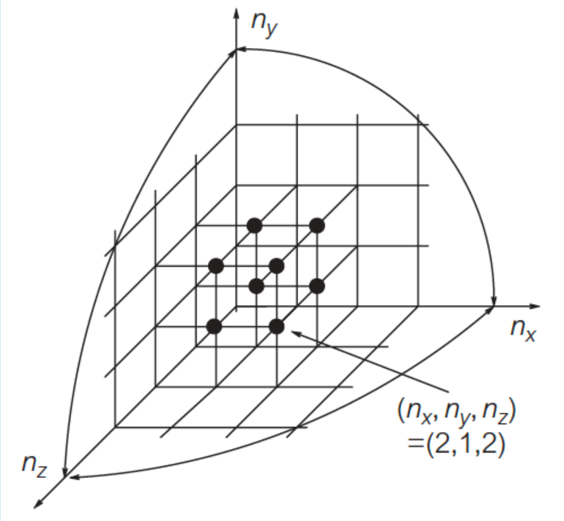
能態的分布還可以用另一個圖像來表示，當量子數大時使用更加方便：

$$\sin\left(\frac{n_x\pi}{L}x\right)\sin\left(\frac{n_y\pi}{L}y\right)\sin\left(\frac{n_z\pi}{L}z\right)$$

一組(n_x, n_y, n_z)對應一個態！

以(n_x, n_y, n_z)畫一空間，一個態即是一個點，在此空間內狀態分佈的密度恰是1！

$\sqrt{n_x^2+n_y^2+n_z^2}$是該點與原點的距離，定義為n。



$$E=\frac{\hbar^2\pi^2}{2mL^2}\left(n_x^2+n_y^2+n_z^2\right)=\frac{\hbar^2\pi^2}{2mL^2}n^2$$

這圖除了定態的分佈，其實點與原點的距離也標示出了定態的能量E。

n^2：與原點的距離平方，恰等於$\frac{2mL^2}{\hbar^2\pi^2}E$。

代表定態的點、距離原點越遠，能量越大！

電子氣是把N個彼此無作用的自由電子放入箱中。

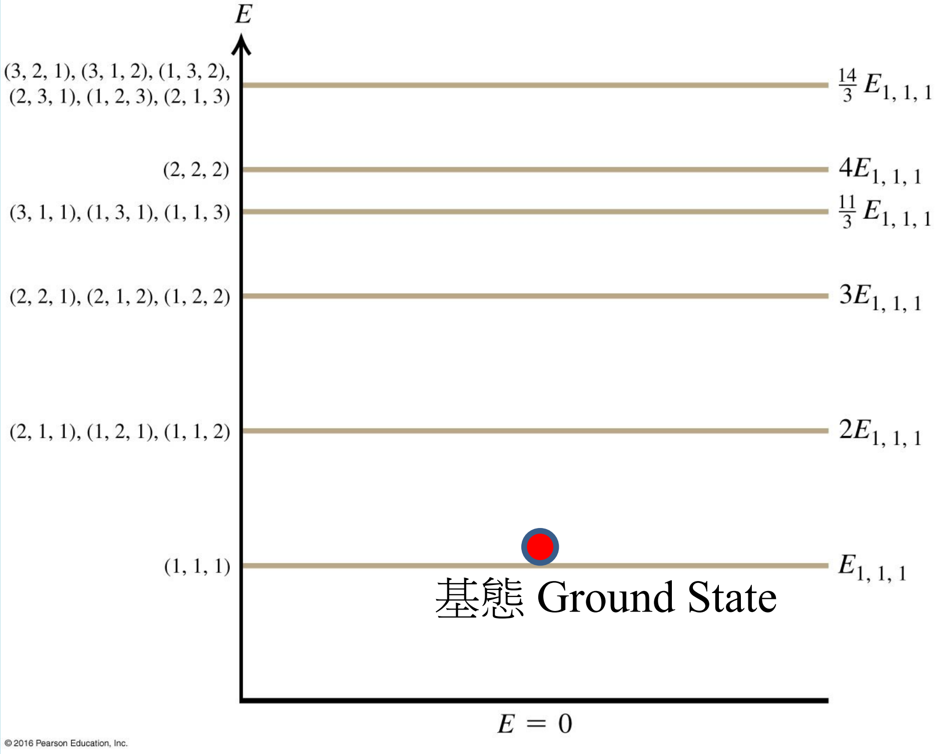
電子彼此無作用，所以電子就會選擇進入以上所得到的單一電子定態。

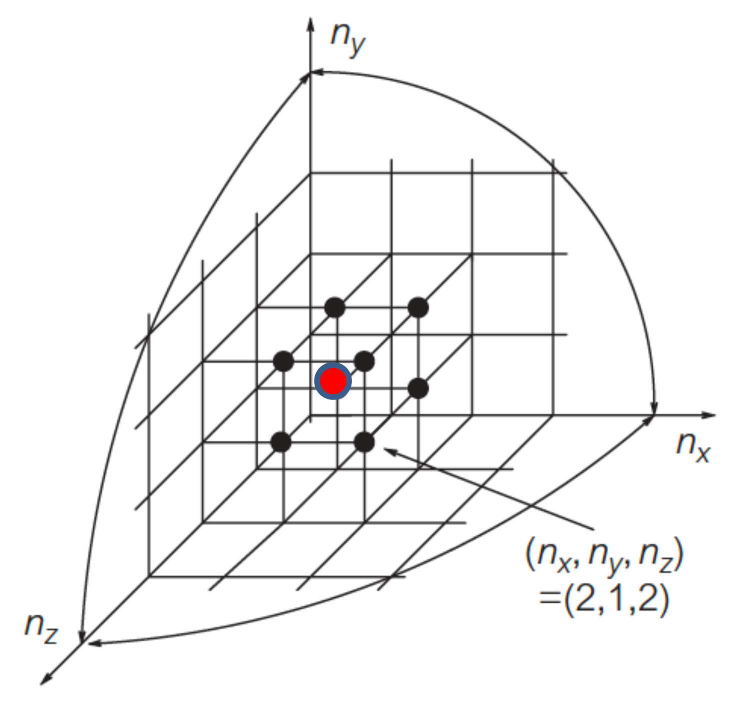
現在問：如果溫度為零，電子的狀態會是如何？

根據波茲曼分佈，

彼此不干擾的古典理想氣體分子個自都會選擇進入能量最低的狀態。

$n_x = n_y = n_z = 1$ 基態 Ground State





電子等費米子卻有奇特的社交規則：

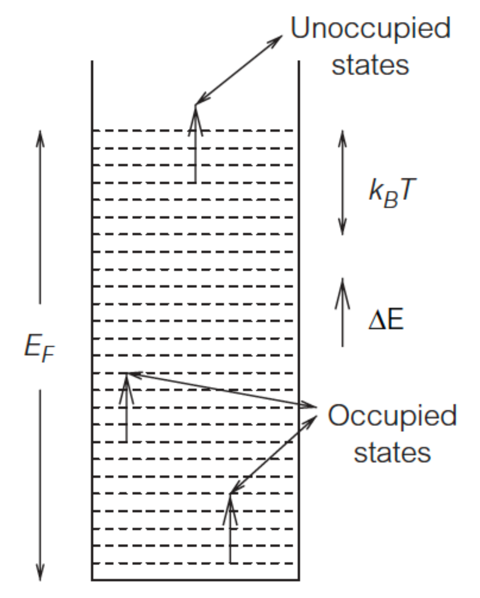
電子滿足不形容原理：兩個電子不能占據同一個量子態。

電子會一個一個由最低的能階向上配置！

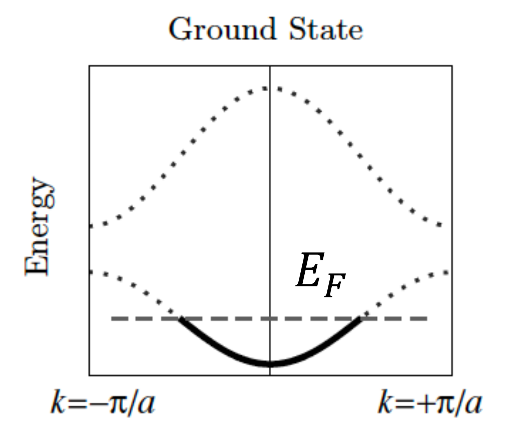
一個量子狀態，只能放置一個電子。

所以彼此不作用的自由電子，彼此卻好像有一個不能忽略的排斥作用。

電子能填到的最高能量，就稱為費米能量Fermi Energy：E_F。



只畫出能量！



之前的一維週期位能也有費米能量。

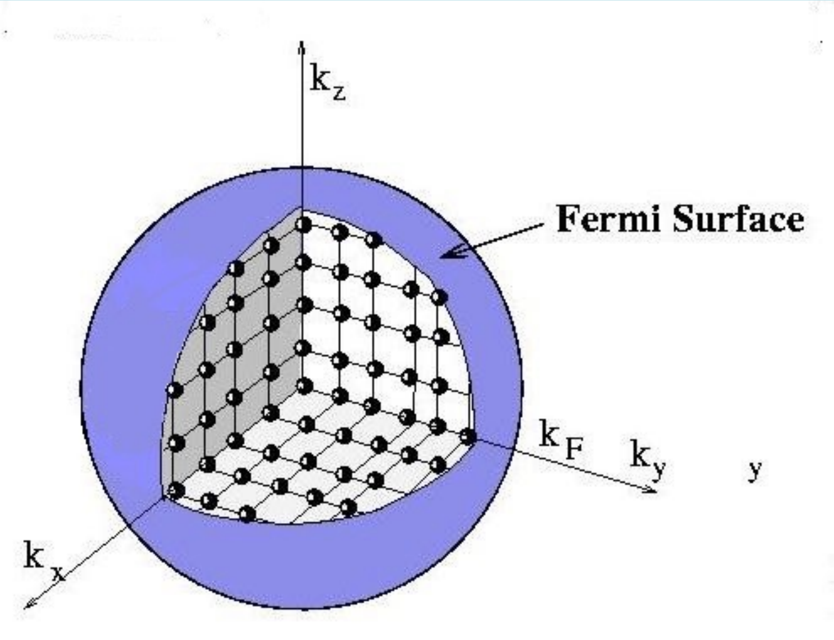
(n_x, n_y, n_z)空間其實也就是(k_x, k_y, k_z)空間！

$$k_x = \frac{\pi}{L} n_x \quad k_y = \frac{\pi}{L} n_y \quad k_z = \frac{\pi}{L} n_z$$

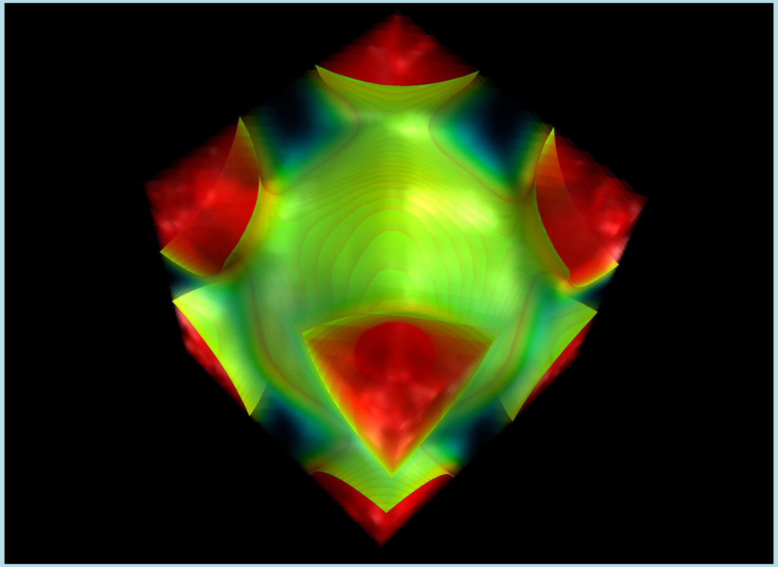
角波數$\vec{k}$是一個向量，標記電子的狀態。

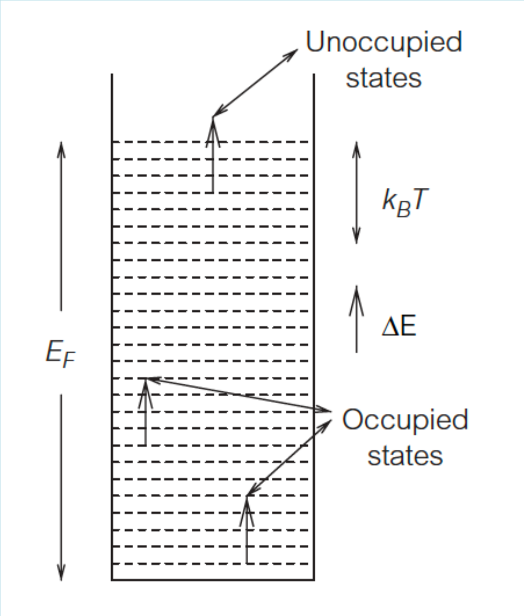
有電子佔據的態就在一個球內！此球面是能量最高的邊界，就稱為費米面！

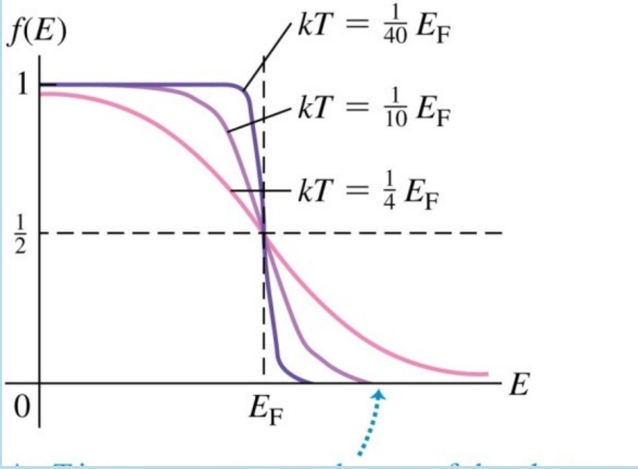
以能量決定的費米面猶如水平面。

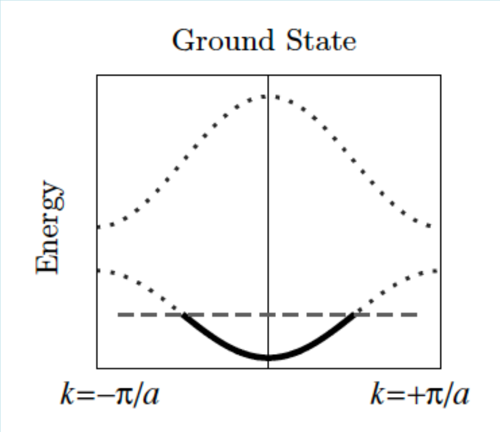


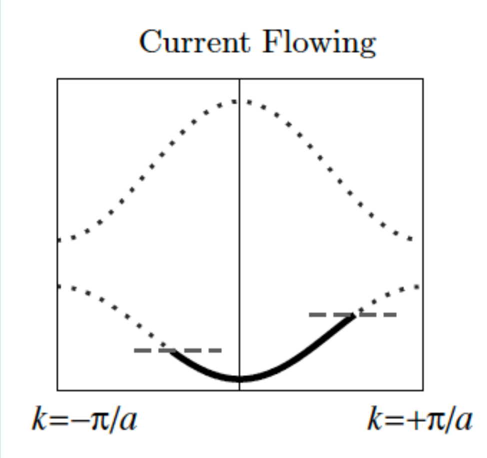
真實晶體中，有時費米面的形狀會很怪。







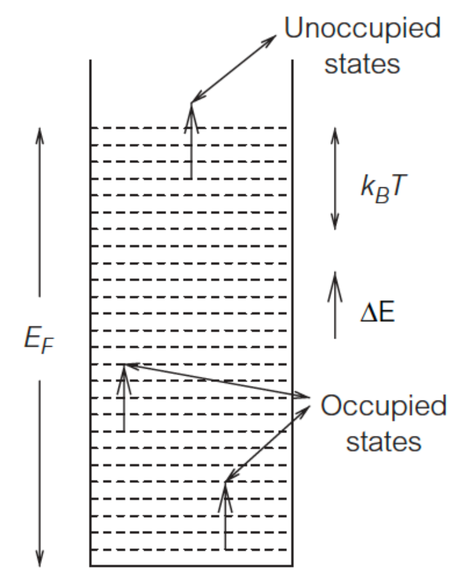




重點是：只有能量略低於E_F的電子才有機會透過加熱或加電場改變狀態！

其餘的電子，改變的機會都已被其他電子佔據。

可見固體的性質，常是由電子在能量接近E_F時的行為所決定！



費米能量E_F的值極重要，它顯然由自由電子個數N決定，

如何由電子個數N計算費米能量E_F？條件：電子狀態能量低於E_F的恰為N個。

能量介在E與$E + dE$之間的電子狀態數：$g(E) \cdot dE$。

$$\int_0^{E_F} dE\, g(E) = N$$

補充教材

已知定態的能量為： $E=\dfrac{\hbar^2\pi^2}{2mL^2}n^2$

計算能量介在E與$E+dE$之間的電子狀態數：$g(E)dE$。

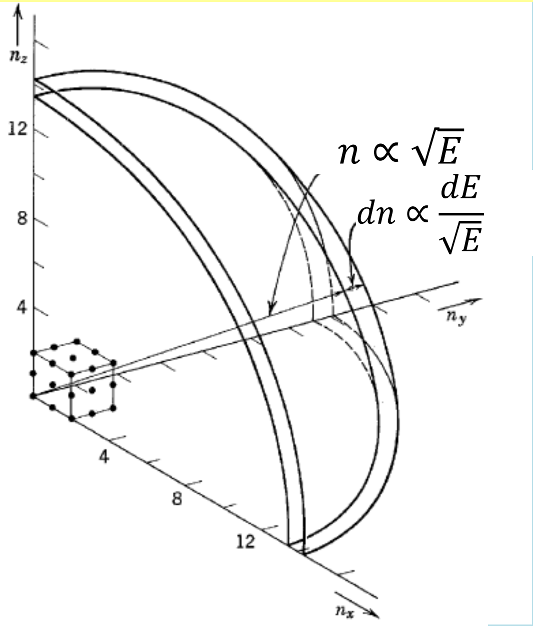
能量介在E與$E+dE$之間的態，代表的點就位於半徑n厚度dn的八分之一球殼內。

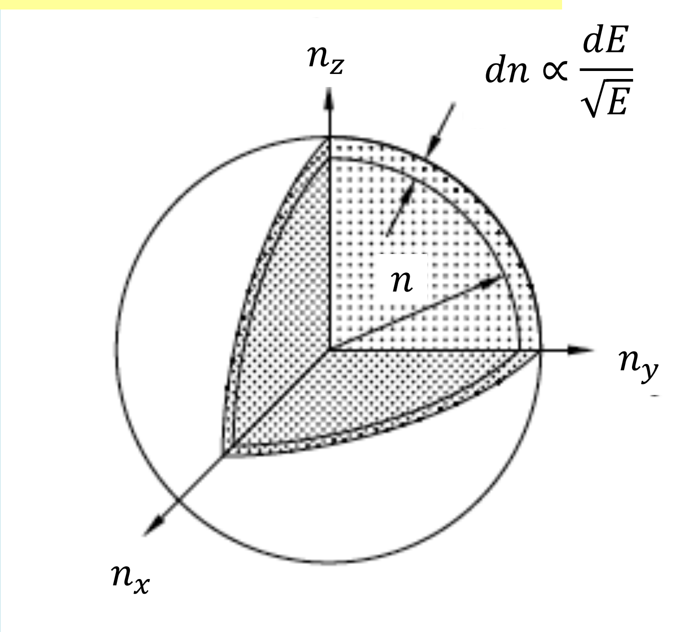
球殼內狀態數目就是球殼體積： $g(E)\cdot dE=\dfrac{2}{8}4\pi n^2\cdot dn$

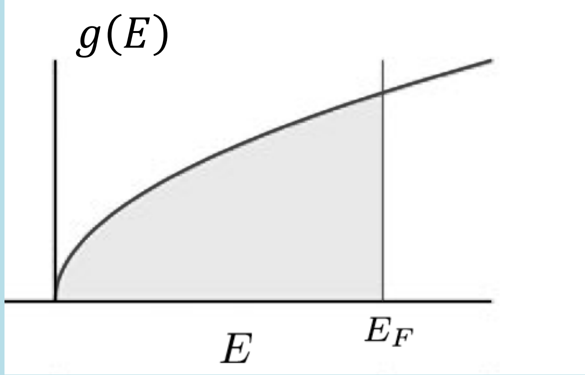
dn與dE有一個簡單關係： $dE=\dfrac{\hbar^2\pi^2}{mL^2}n\cdot dn$

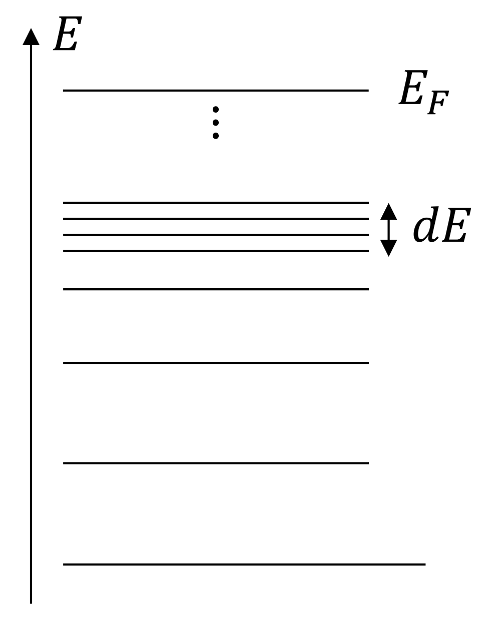
$$\frac{2}{8}4\pi n^2\cdot dn=\sqrt{\frac{mL^2}{\hbar^2\pi^2}}\pi n\cdot dE=\frac{\sqrt{2}m^{3/2}V}{\hbar^3\pi^2}\sqrt{E}dE$$

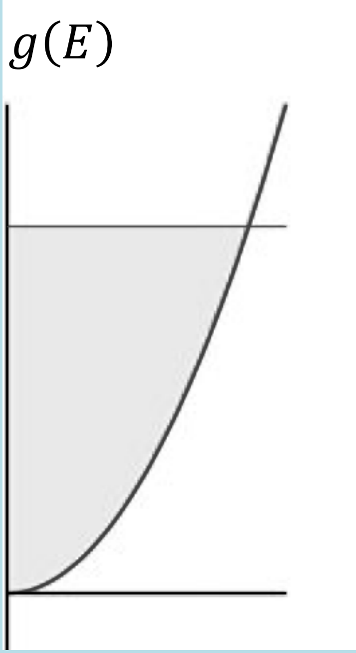
$$g(E)=\frac{\sqrt{2}m^{3/2}V}{\hbar^3\pi^2}\sqrt{E}$$











E_F可以直接用狀態密度$g(E)$直接算：

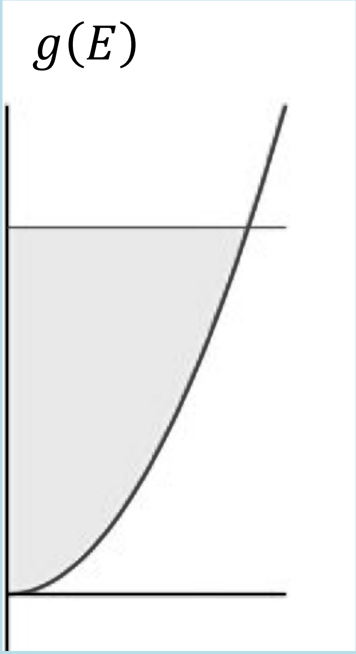
$$\int_0^{E_F} dE\, g(E) = \int_0^{E_F} dE\, \frac{\sqrt{2}m^{3/2}V}{\hbar^3\pi^2}\sqrt{E} = \frac{\sqrt{2}m^{3/2}V}{\hbar^3\pi^2}\int_0^{E_F} dE\,\sqrt{E} = N$$

$$= \frac{2\sqrt{2}m^{3/2}V}{3\hbar^3\pi^2}E_F^{\frac{3}{2}} = N$$

能量低於費米能量E_F的能態的數目乘2就是電子個數N。

$$E_F = \frac{\hbar^2\pi^2}{2m}\left(\frac{3}{\pi}\frac{N}{V}\right)^{\frac{2}{3}} = \frac{\hbar^2\pi^2}{2m}\left(\frac{3}{\pi}n_e\right)^{\frac{2}{3}}$$

$$n_e \equiv \frac{N}{V}$$



$$E_F = \frac{\hbar^2\pi^2}{2m}\left(\frac{3}{\pi}\frac{N}{V}\right)^{\frac{2}{3}} = \frac{\hbar^2\pi^2}{2m}\left(\frac{3}{\pi}n_e\right)^{\frac{2}{3}}$$

$$n_e \equiv \frac{N}{V}$$

$T = 0,$時E_F由單位體積電子數決定。

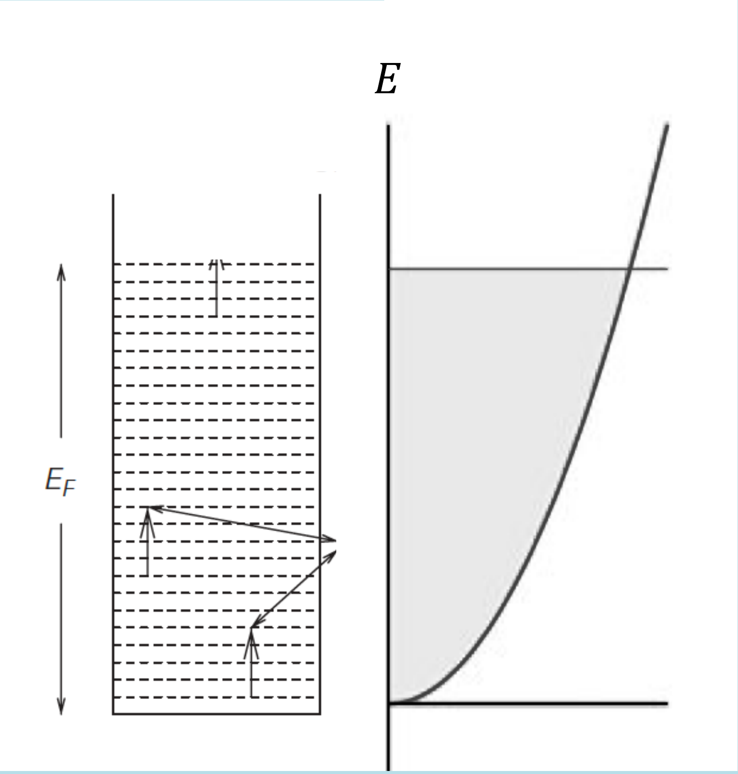
以銅為例，代入n_e， $E_F \sim 7\ \mathrm{eV} \sim k \cdot 80000\ \mathrm{K}$　費米能量高達80000度的熱能。
電子速度高達$0.1c$。

這表示電子氣在溫度為零，能量最低時，電子必然是充滿動能！
民主的活力？☺　量子驚奇！

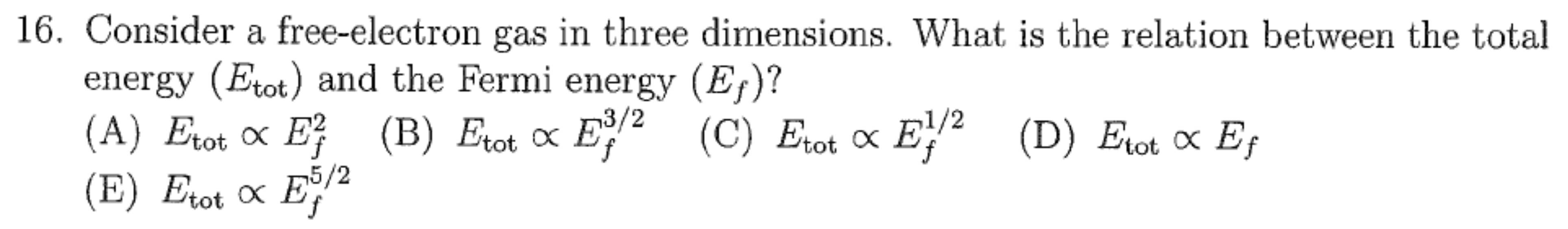
補充教材

總能量也可以直接用$g(E)$狀態密度計算：

$$E_{\text{Total}} = \int_0^{E_F} g(E)dE \cdot E = \int_0^{E_F} dE \cdot \frac{\sqrt{2}m^{3/2}}{\hbar^3\pi^2} E^{\frac{3}{2}} = \frac{2\sqrt{2}m^{3/2}}{5\hbar^3\pi^2} E_F^{\frac{5}{2}}$$



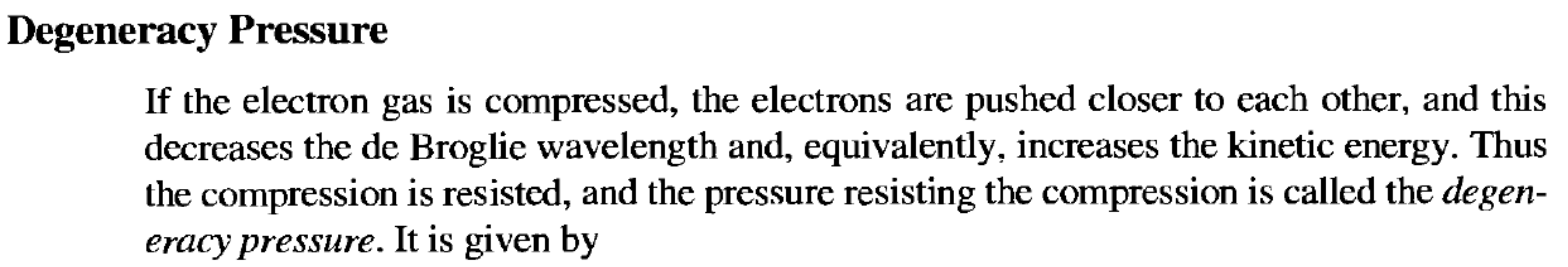
$$g(E) = \frac{\sqrt{2}m^{3/2}}{\hbar^3\pi^2}\sqrt{E}$$



16. Consider a free-electron gas in three dimensions. What is the relation between the total energy (E_{tot}) and the Fermi energy (E_f)?

(A) $E_{\text{tot}} \propto E_f^2$ (B) $E_{\text{tot}} \propto E_f^{3/2}$ (C) $E_{\text{tot}} \propto E_f^{1/2}$ (D) $E_{\text{tot}} \propto E_f$

(E) $E_{\text{tot}} \propto E_f^{5/2}$



Degeneracy Pressure

If the electron gas is compressed, the electrons are pushed closer to each other, and this decreases the de Broglie wavelength and, equivalently, increases the kinetic energy. Thus the compression is resisted, and the pressure resisting the compression is called the *degeneracy pressure*. It is given by

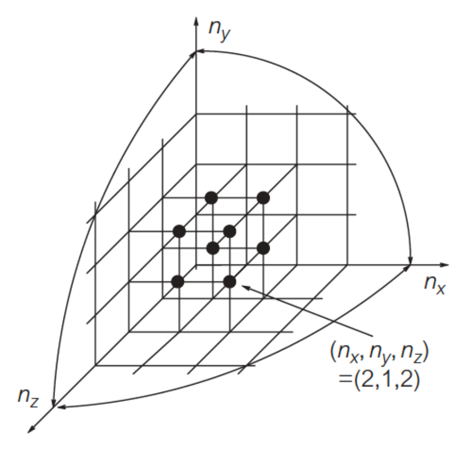
$$E_{\text{Total}} \propto V^{-\frac{2}{3}}$$

能量隨體積減少而變大，壓縮電子氣會增加其內能。

可見電子氣如理想氣體一般，有一個對外的壓力！

$$E_{\text{Total}} = \frac{\hbar^2\pi^3}{10m}\left(\frac{3}{\pi}N\right)^{\frac{5}{3}} V^{-\frac{2}{3}}$$

$$P = -\frac{\partial E_{\text{Total}}}{\partial V} = \frac{\hbar^2\pi^3}{15m}\left(\frac{3}{\pi}\frac{N}{V}\right)^{\frac{5}{3}}$$



壓力由單位體積電子數決定：$n_e = \dfrac{N}{V}$

壓力與體積滿足特定關係：

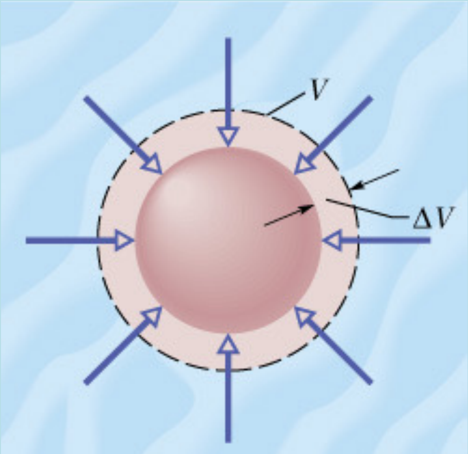
補充教材

$$PV^{\frac{5}{3}} = \frac{\hbar^2\pi^3}{15m}\left(\frac{3}{\pi}N\right)^{\frac{5}{3}}$$

右邊是常數，這就是電子氣溫度為零時的狀態方程式！

這是可以測量驗證的。

物質的體積變化比例與壓力變化成正比！



$$\Delta P = -B \cdot \frac{\Delta V}{V}$$

B是體積彈性係數Bulk Modulus

$$P = nRT \cdot V^{-1}$$

等溫理想氣體

$$B = -\frac{dP}{dV} \cdot V = nRTV^{-1} = P$$

$$P = c \cdot V^{-\gamma}$$

絕熱理想氣體

補充教材

$$B = -\frac{dP}{dV} \cdot V = \gamma c V^{-\gamma} = \gamma P = 1.4P$$

$$B = 1.4P$$

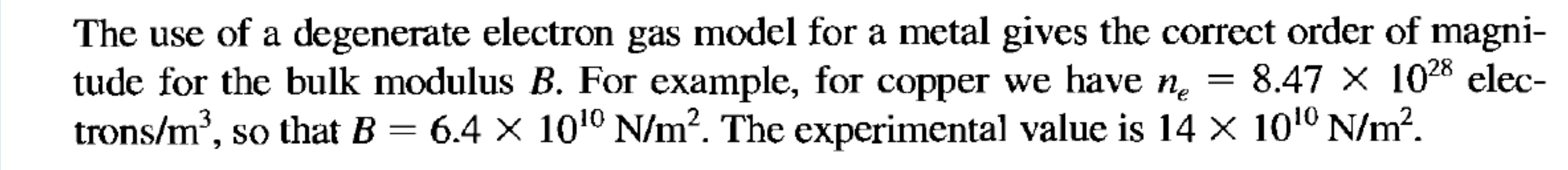
$$PV^{\frac{5}{3}} = c$$

電子氣的狀態方程式！

$$B = -\frac{dP}{dV} \cdot V = -\frac{d}{dV} cV^{-\frac{5}{3}} \cdot V = c\frac{5}{3}V^{-\frac{5}{3}} = \frac{5}{3}P$$

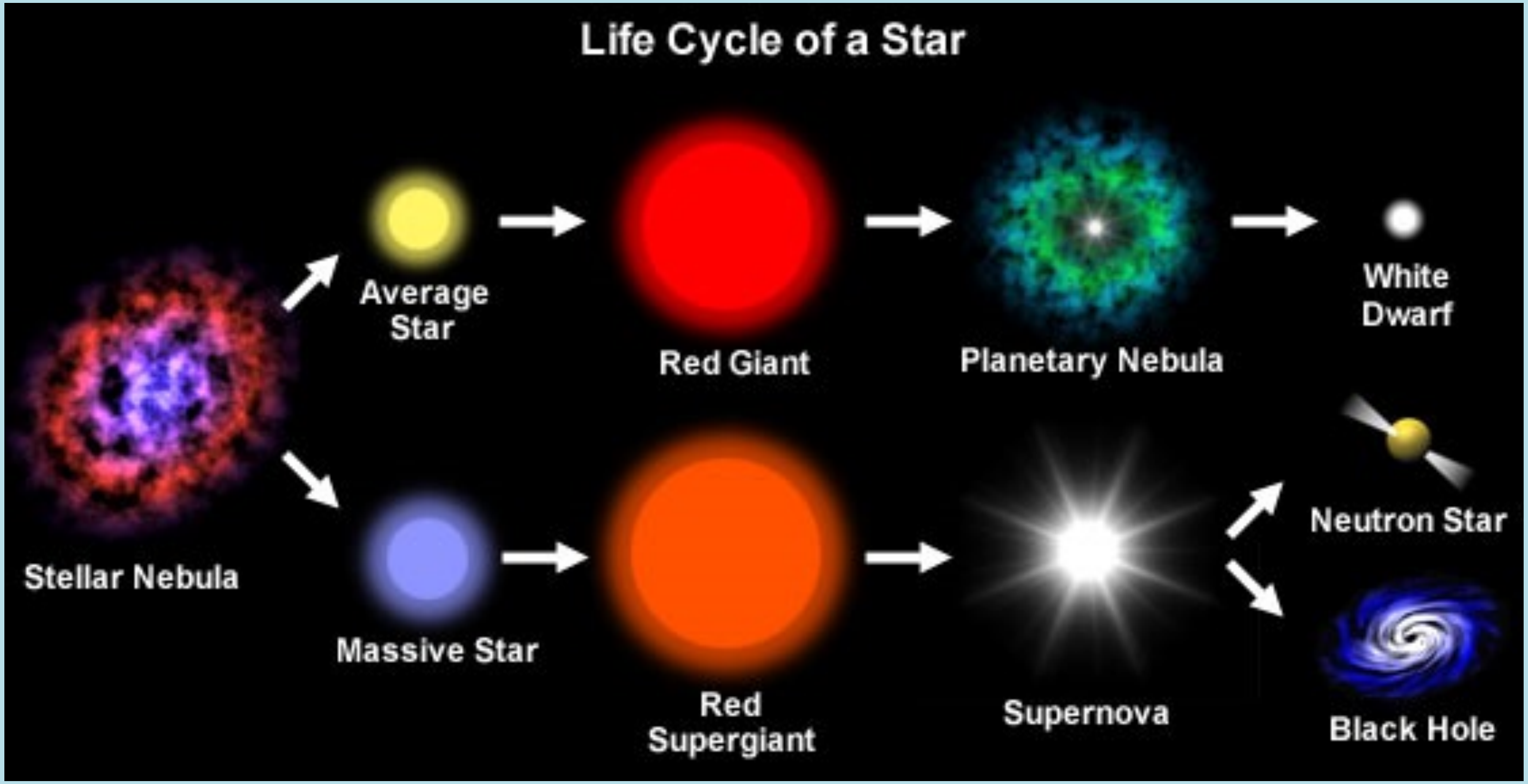
$$B = \frac{5}{3}P = \frac{\hbar^2\pi^3}{9m}\left(\frac{3}{\pi}n\right)^{\frac{5}{3}}$$

體積彈性係數也由單位體積電子數決定。

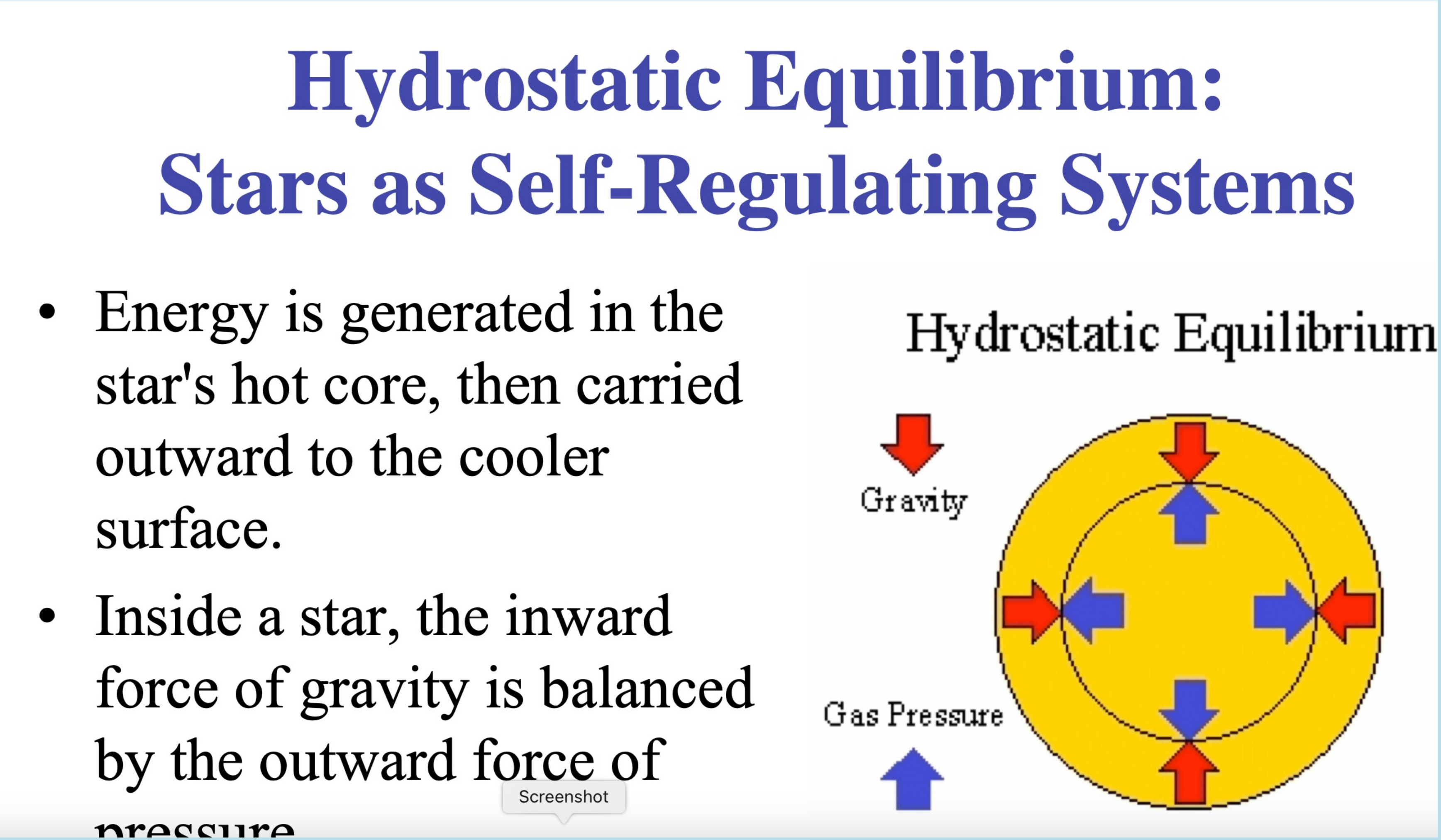


The use of a degenerate electron gas model for a metal gives the correct order of magnitude for the bulk modulus B. For example, for copper we have $n_e = 8.47 \times 10^{28}$ electrons/m^3, so that $B = 6.4 \times 10^{10}$ N/m^2. The experimental value is 14×10^{10} N/m^2.

Degeneracy Pressure決定了星球演化的終點！



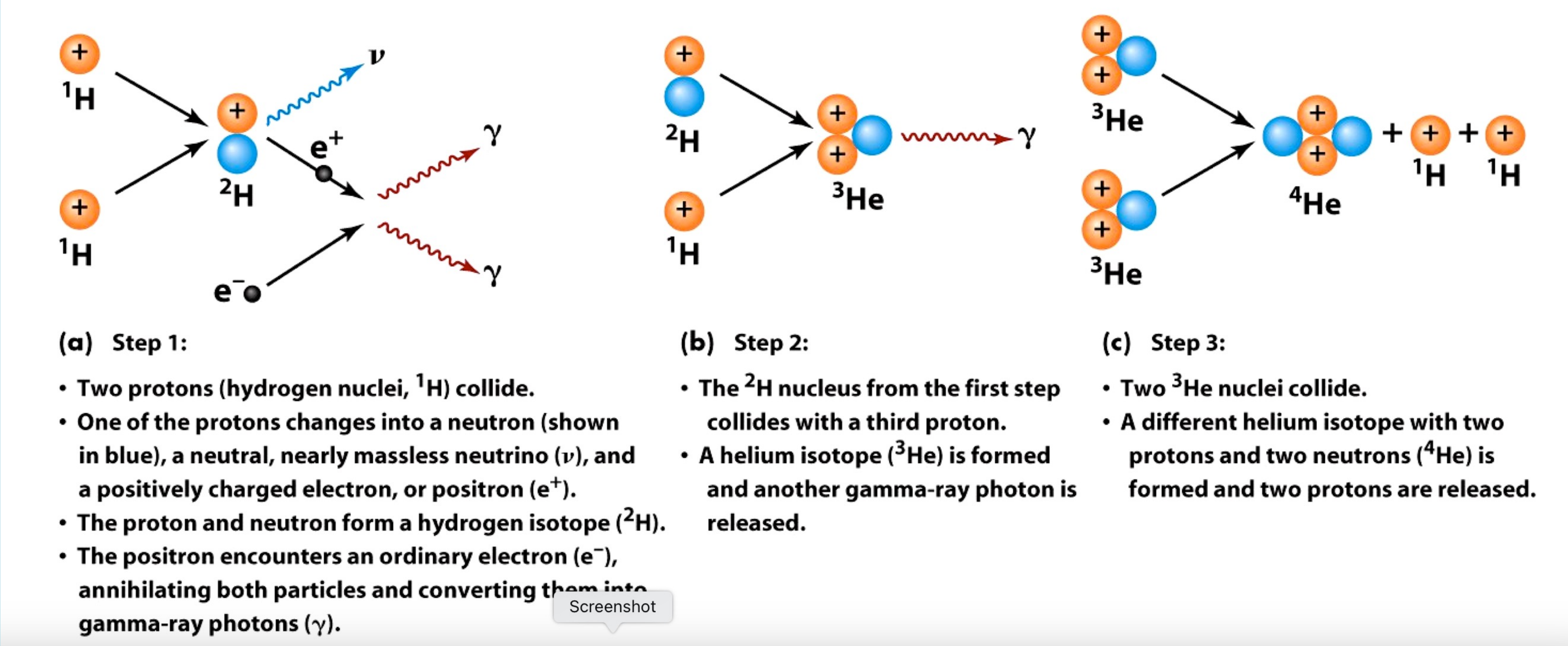
恆星核融合產生高溫下的氣體壓力，與重力製造的向內壓力彼此平衡。



Hydrostatic Equilibrium: Stars as Self-Regulating Systems

- Energy is generated in the star's hot core, then carried outward to the cooler surface.
- Inside a star, the inward force of gravity is balanced by the outward force of pressure

The main process is hydrogen fusion into helium:



(a) Step 1:

- Two protons (hydrogen nuclei, ^{1}H) collide.
- One of the protons changes into a neutron (shown in blue), a neutral, nearly massless neutrino (ν), and a positively charged electron, or positron (e^+).
- The proton and neutron form a hydrogen isotope (^{2}H).
- The positron encounters an ordinary electron (e^-), annihilating both particles and converting them into gamma-ray photons (γ).

(b) Step 2:

- The ^{2}H nucleus from the first step collides with a third proton.
- A helium isotope (^{3}He) is formed and another gamma-ray photon is released.

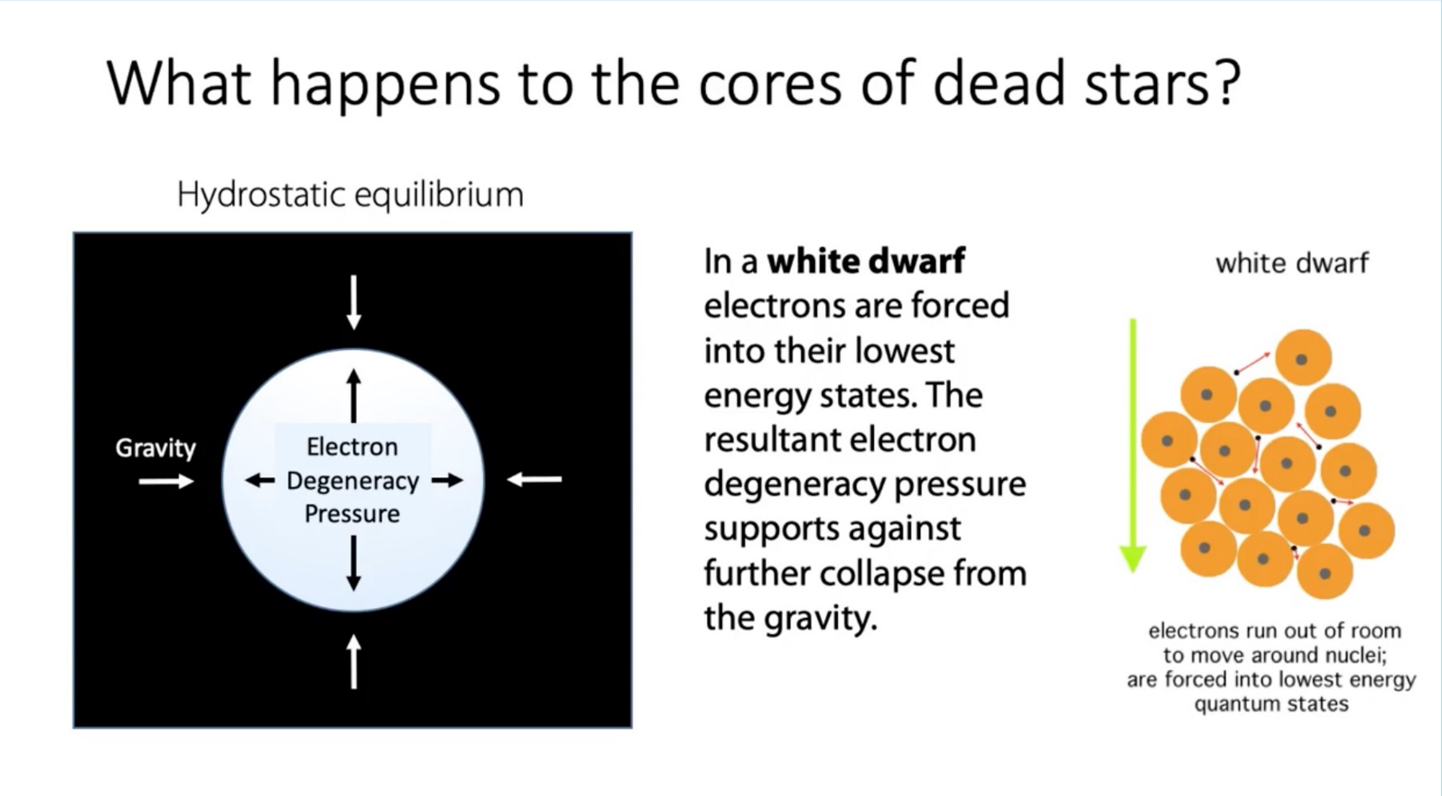
(c) Step 3:

- Two ^{3}He nuclei collide.
- A different helium isotope with two protons and two neutrons (^{4}He) is formed and two protons are released.

死亡的恆星已無核融合，塌陷後，電子被壓縮進入最低能量狀態，

最低能量態因電子的不相容原理，竟然會抗拒繼續的壓縮！

Degeneracy Pressure 與重力製造的向內壓力彼此平衡，以致不再繼續塌陷。



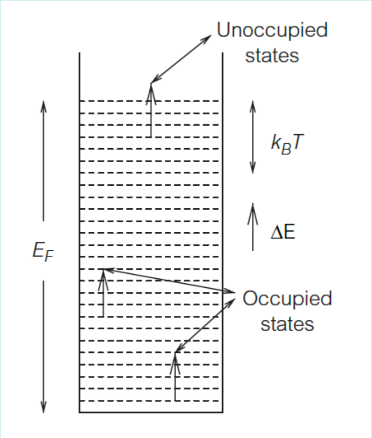
What happens to the cores of dead stars?

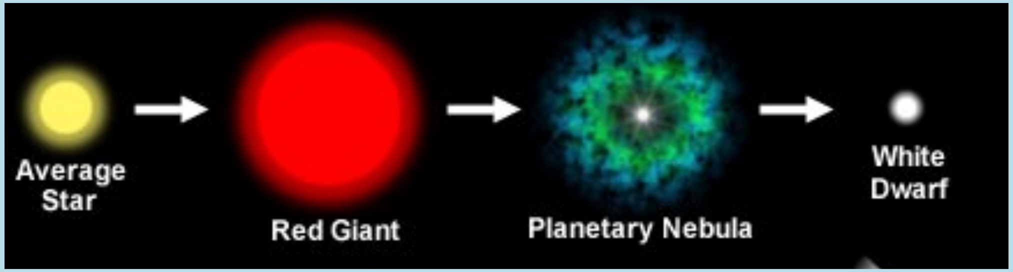
Hydrostatic equilibrium

In a **white dwarf** electrons are forced into their lowest energy states. The resultant electron degeneracy pressure supports against further collapse from the gravity.

white dwarf

electrons run out of room to move around nuclei; are forced into lowest energy quantum states





我們可以估計白矮星的半徑：

先估計星球的重力位能與對應的壓力，假設是球形質量分佈，密度均勻ρ。

$$dV_G = -G\frac{\rho 4\pi r^2}{r}\rho\frac{4}{3}\pi r^3 dr$$

—球殼位能

$$V_G = -\frac{(4\pi)^2 G\rho^2}{3}\int_0^R dr\, r^4 dr = -\frac{(4\pi)^2 G\rho^2}{15}R^5$$

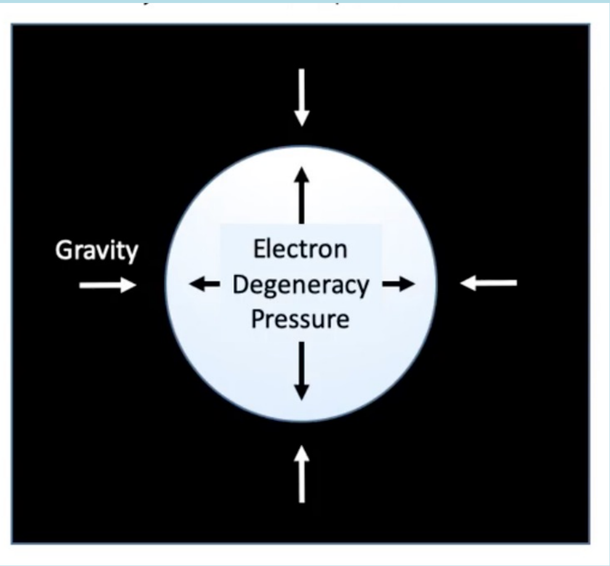
代入：$\rho\frac{4}{3}\pi R^3 = Nm_N$

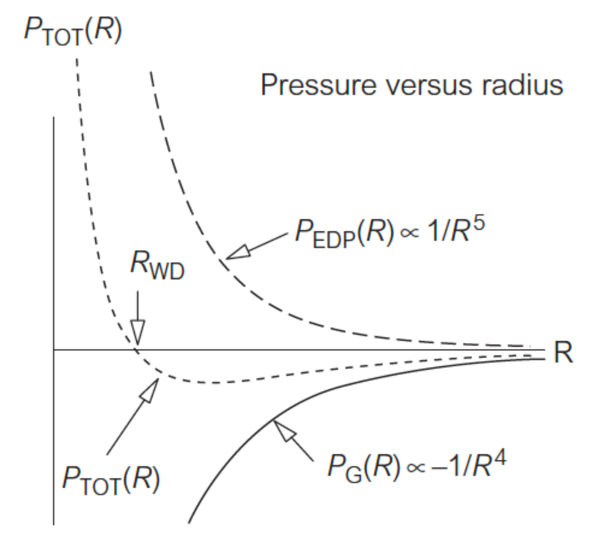
$$V_G = -\frac{3}{5}\left(\frac{4\pi}{3}\right)^{\frac{1}{3}} G(Nm_N)^2 V^{-\frac{1}{3}}$$

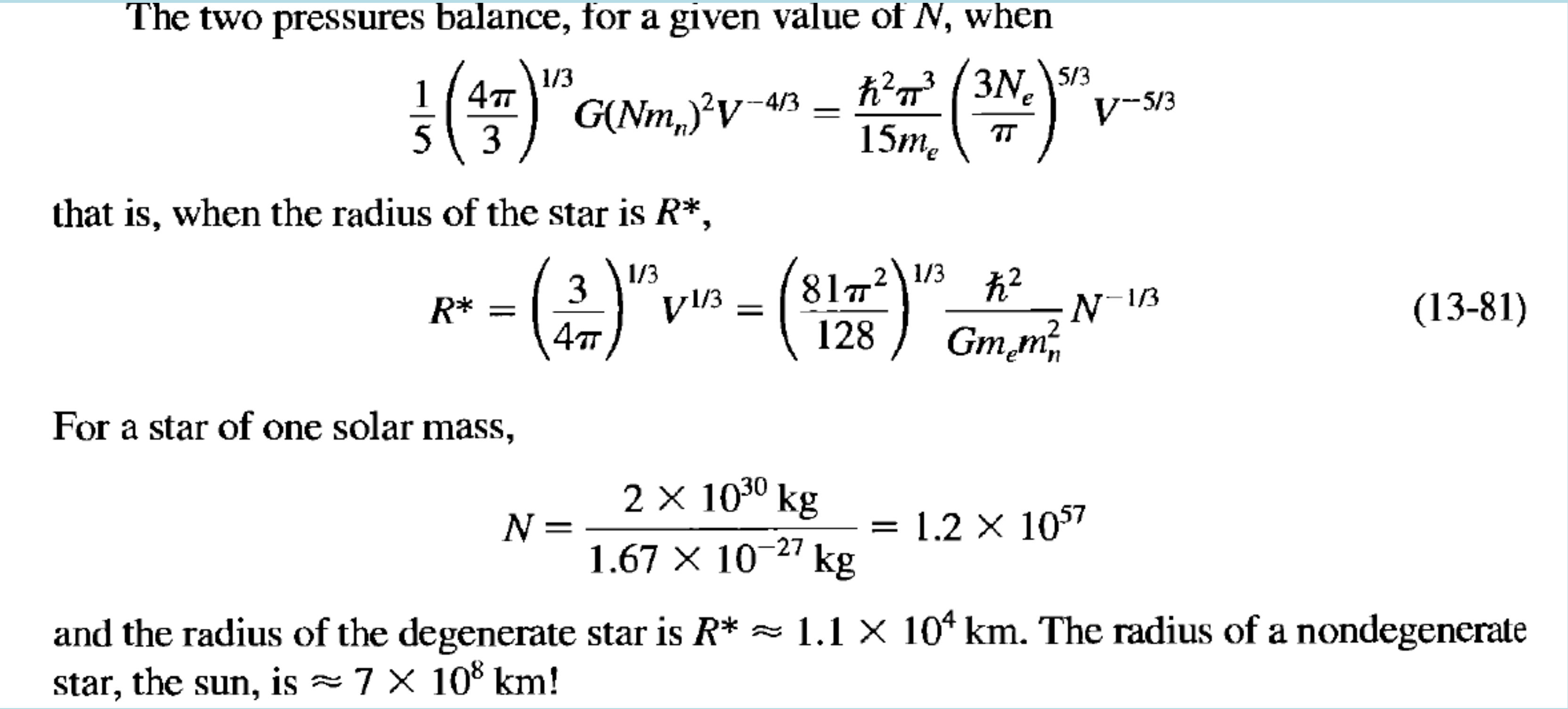
$$P_G = -\frac{\partial V_G}{\partial V} = \frac{1}{5}\left(\frac{4\pi}{3}\right)^{\frac{1}{3}} G(Nm_N)^2 V^{-\frac{4}{3}}$$

壓力平衡時：

$$\frac{\hbar^2\pi^3}{15m_e}\left(\frac{3}{\pi}N_e\right)^{\frac{5}{3}} V^{-\frac{5}{3}} = \frac{1}{5}\left(\frac{4\pi}{3}\right)^{\frac{1}{3}} G(Nm_N)^2 V^{-\frac{4}{3}}$$







The two pressures balance, for a given value of N, when

$$\frac{1}{5}\left(\frac{4\pi}{3}\right)^{1/3} G(Nm_n)^2 V^{-4/3} = \frac{\hbar^2\pi^3}{15m_e}\left(\frac{3N_e}{\pi}\right)^{5/3} V^{-5/3}$$

that is, when the radius of the star is R^*,

$$R^* = \left(\frac{3}{4\pi}\right)^{1/3} V^{1/3} = \left(\frac{81\pi^2}{128}\right)^{1/3} \frac{\hbar^2}{Gm_e m_n^2} N^{-1/3} \tag{13-81}$$

For a star of one solar mass,

$$N = \frac{2 \times 10^{30}\ \mathrm{kg}}{1.67 \times 10^{-27}\ \mathrm{kg}} = 1.2 \times 10^{57}$$

and the radius of the degenerate star is $R^* \approx 1.1 \times 10^4$ km. The radius of a nondegenerate star, the sun, is $\approx 7 \times 10^8$ km!

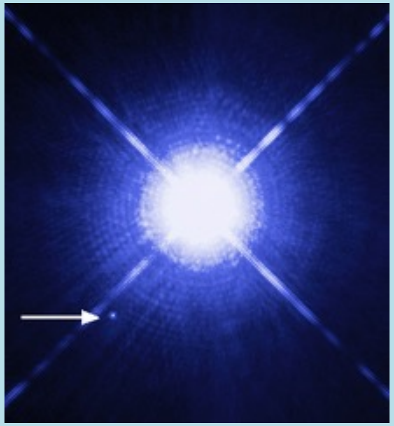
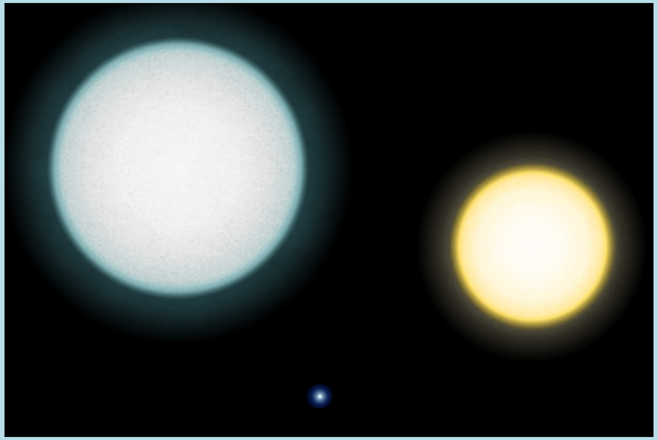
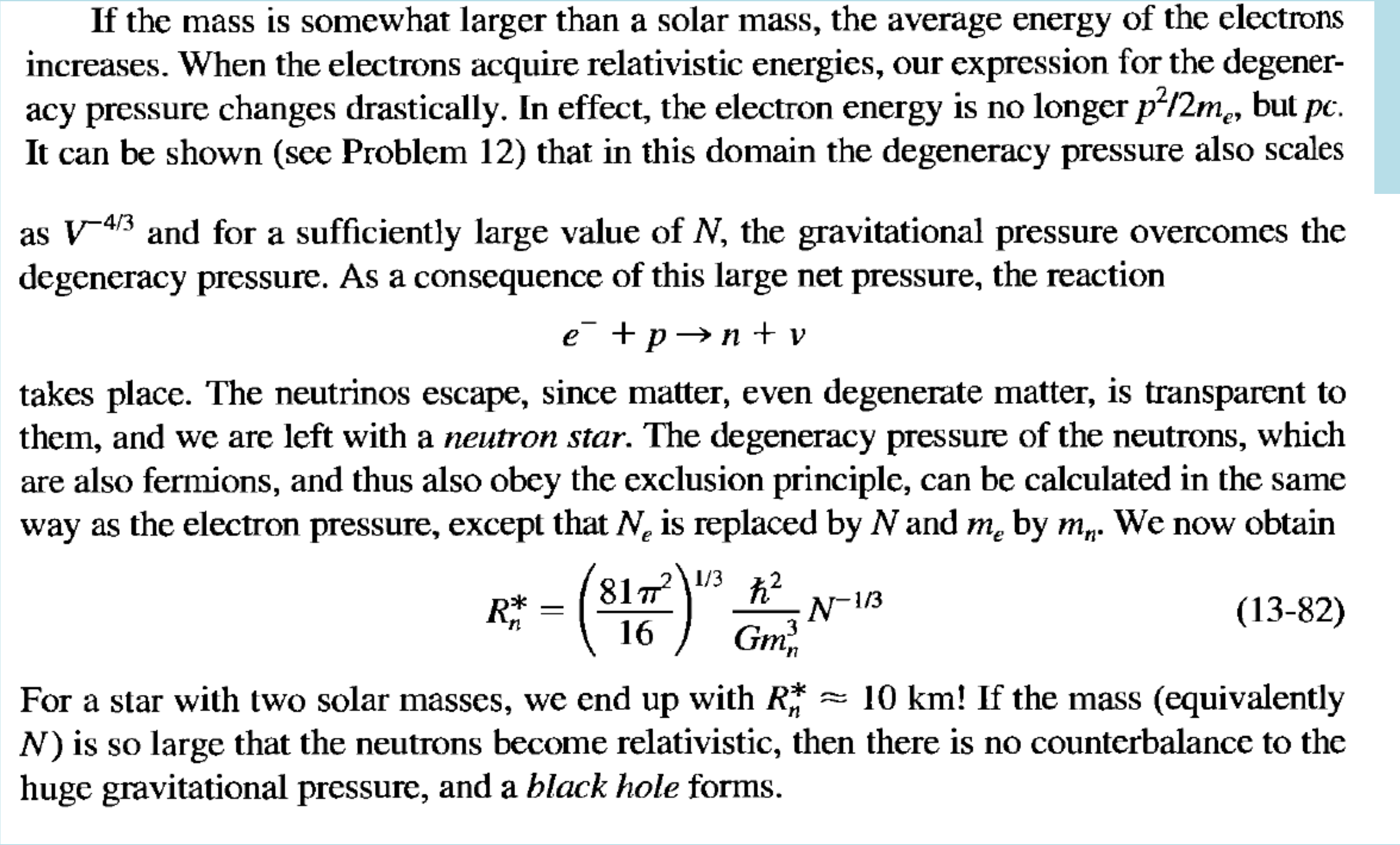


Image of Sirius A and Sirius B taken by the Hubble Space Telescope. Sirius B, which is a white dwarf, can be seen as a faint point of light to the lower left of the much brighter Sirius A.



A comparison between the white dwarf IK Pegasi B (center), its A-class companion IK Pegasi A (left) and the Sun (right). This white dwarf has a surface temperature of 35,500 K



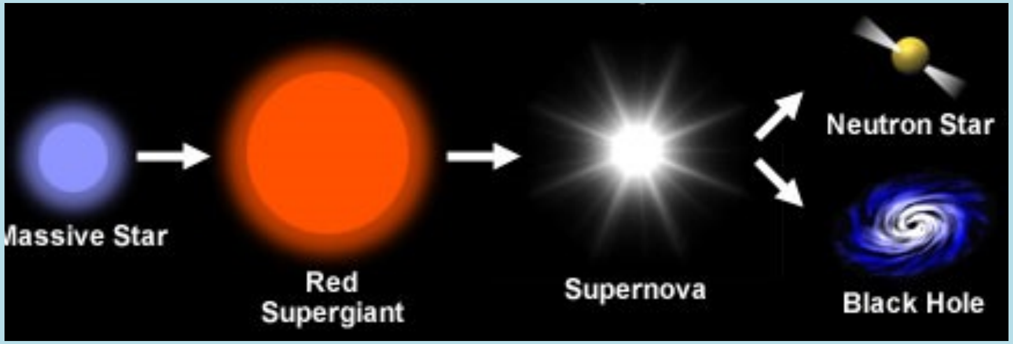
If the mass is somewhat larger than a solar mass, the average energy of the electrons increases. When the electrons acquire relativistic energies, our expression for the degeneracy pressure changes drastically. In effect, the electron energy is no longer $p^2/2m_e$, but pc. It can be shown (see Problem 12) that in this domain the degeneracy pressure also scales as $V^{-4/3}$ and for a sufficiently large value of N, the gravitational pressure overcomes the degeneracy pressure. As a consequence of this large net pressure, the reaction

$$e^- + p \rightarrow n + \nu$$

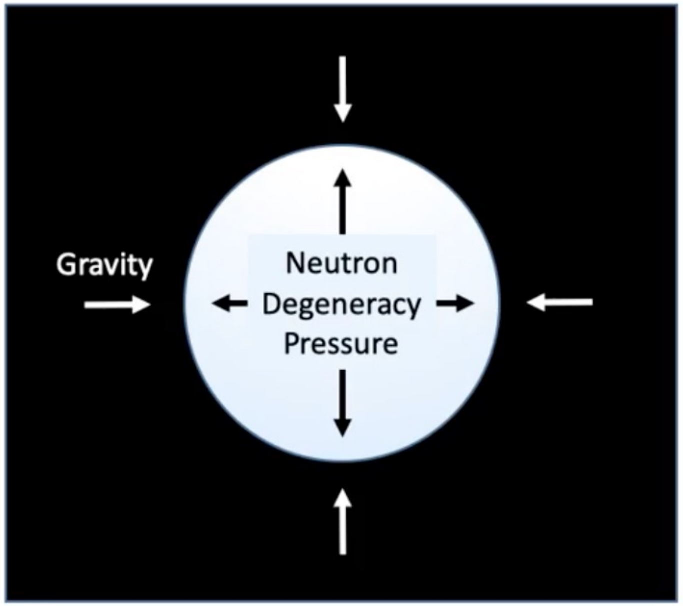
takes place. The neutrinos escape, since matter, even degenerate matter, is transparent to them, and we are left with a *neutron star*. The degeneracy pressure of the neutrons, which are also fermions, and thus also obey the exclusion principle, can be calculated in the same way as the electron pressure, except that N_e is replaced by N and m_e by m_n. We now obtain

$$R_n^* = \left(\frac{81\pi^2}{16}\right)^{1/3} \frac{\hbar^2}{Gm_n^3} N^{-1/3} \tag{13-82}$$

For a star with two solar masses, we end up with $R_n^* \approx 10$ km! If the mass (equivalently N) is so large that the neutrons become relativistic, then there is no counterbalance to the huge gravitational pressure, and a *black hole* forms.

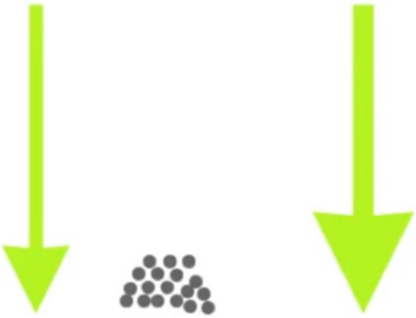


Hydrostatic equilibrium



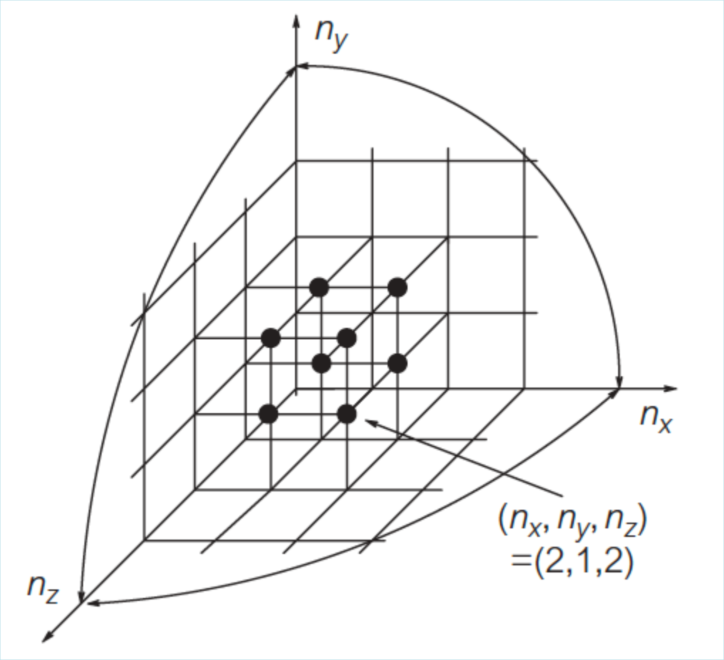
In a **neutron star** electrons are squeezed into the protons, creating a neutron superfluid, probably with an iron crust. Neutron degeneracy pressure supports against further collapse due to gravity.

neutron star



protons are forced to absorb electrons to make neutrons; neutrons squeezed together

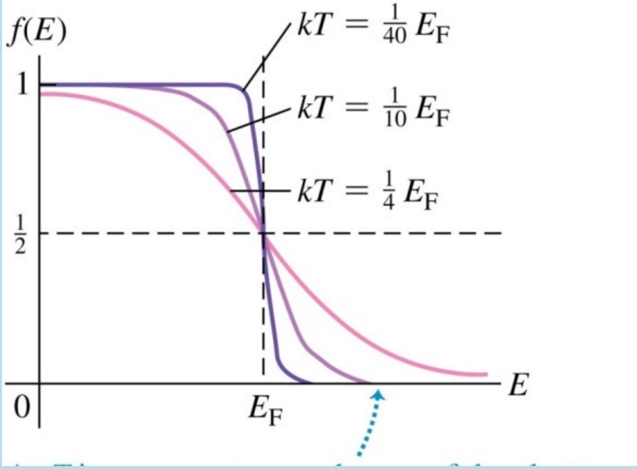
接著可以為電子氣加上電場，增加溫度。



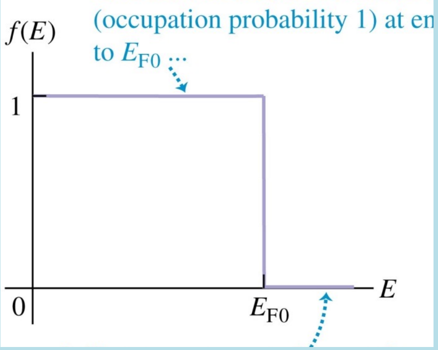
根據費米統計，理想電子氣體，處在一特定溫度T、特定化學能μ環境中，

一個能量為E的能態的平均粒子數等於Fermi-Dirac Factor：

$$n_F(E) = \frac{1}{e^{\frac{(E-\mu)}{kT}} + 1}$$



$T = 0$



平均粒子數由能量決定，對狀態加總以$g(E)$狀態密度(能量函數)、E積分最方便：

$$N = \int_0^\infty dE \cdot g(E) \cdot n_F(E)$$

此式可以由已知的N值得出Chemical Potential μ。

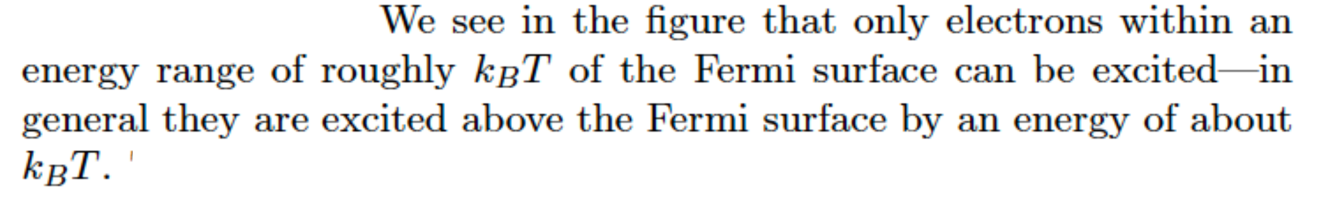
總能量E_{Total}即是狀態的能量、乘狀態密度，乘費米統計，再加總至無限大：

$$E_{\text{Total}} = \int_0^\infty dE \cdot E \cdot g(E) \cdot n_F(E)$$

導體熱性質例如比熱c_V就可以推導出來！

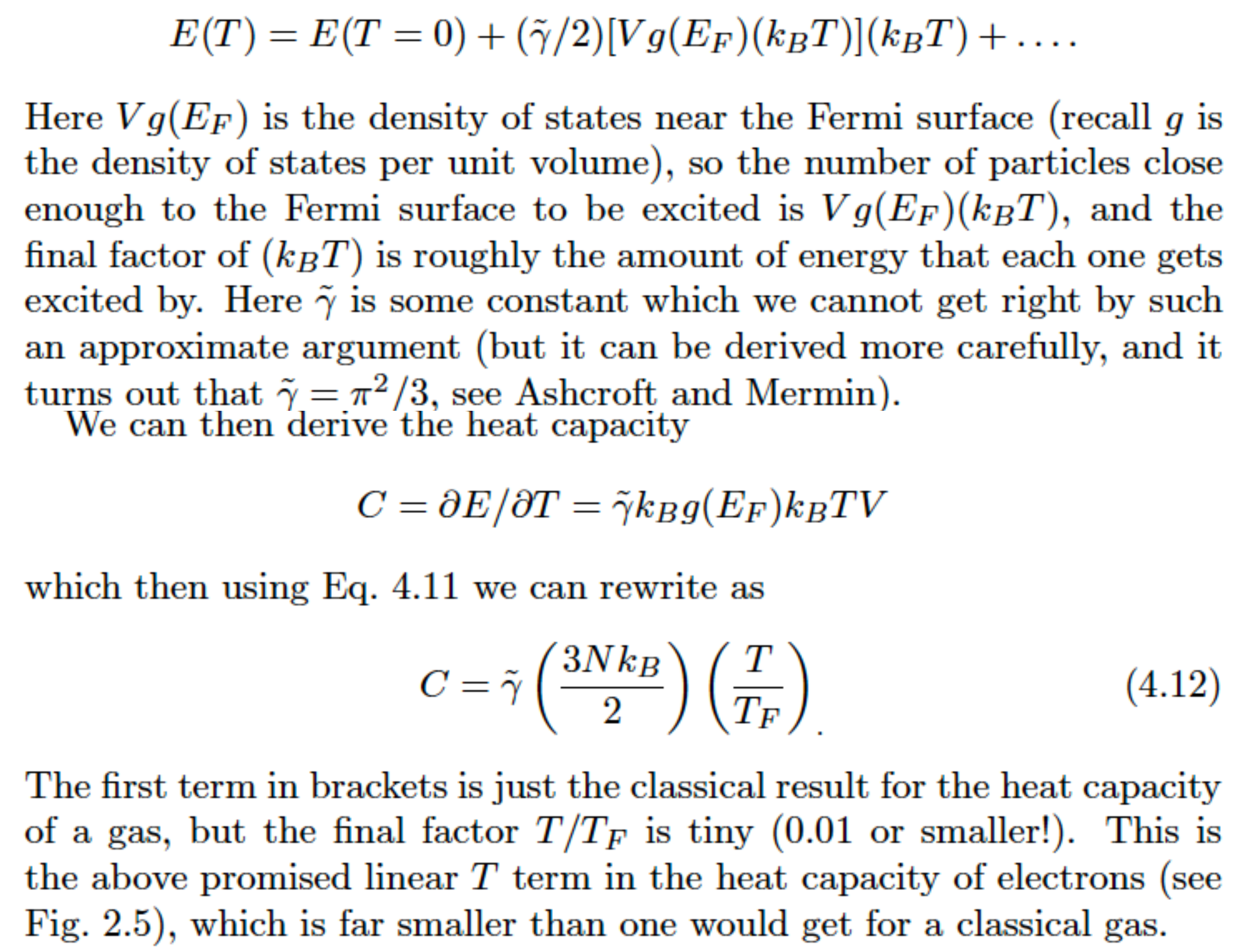
但一般來說，此式較難直接計算，而用近似。

小於費米能量$E \ll E_F$的狀態，加溫後不會有改變！



We see in the figure that only electrons within an energy range of roughly $k_B T$ of the Fermi surface can be excited—in general they are excited above the Fermi surface by an energy of about $k_B T$.

近似來說，加溫後能量變化來自費米能量前後、能差約kT範圍內的這些狀態：



$$E(T) = E(T=0) + (\tilde{\gamma}/2)[Vg(E_F)(k_B T)](k_B T) + \ldots .$$

Here $Vg(E_F)$ is the density of states near the Fermi surface (recall g is the density of states per unit volume), so the number of particles close enough to the Fermi surface to be excited is $Vg(E_F)(k_B T)$, and the final factor of $(k_B T)$ is roughly the amount of energy that each one gets excited by. Here $\tilde{\gamma}$ is some constant which we cannot get right by such an approximate argument (but it can be derived more carefully, and it turns out that $\tilde{\gamma} = \pi^2/3$, see Ashcroft and Mermin).

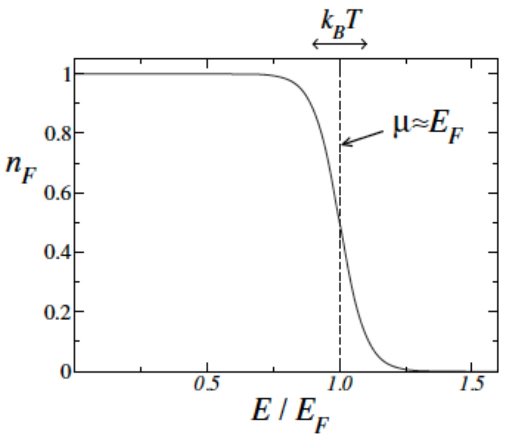
We can then derive the heat capacity

$$C = \partial E/\partial T = \tilde{\gamma} k_B g(E_F) k_B T V$$

which then using Eq. 4.11 we can rewrite as

$$C = \tilde{\gamma} \left(\frac{3Nk_B}{2} \right) \left(\frac{T}{T_F} \right) . \qquad (4.12)$$

The first term in brackets is just the classical result for the heat capacity of a gas, but the final factor T/T_F is tiny (0.01 or smaller!). This is the above promised linear T term in the heat capacity of electrons (see Fig. 2.5), which is far smaller than one would get for a classical gas.



More Electrons in Metals: Sommerfeld (Free Electron) Theory

4

In 1925 Pauli discovered the exclusion principle, that no two electrons may be in the exact same state. In 1926, Fermi and Dirac separately derived what we now call Fermi–Dirac statistics.[1] Upon learning about these developments, Sommerfeld[2] realized that Drude's theory of metals could easily be generalized to incorporate Fermi statistics, which is what we shall presently do.

4.1 Basic Fermi–Dirac Statistics

Given a system of free[3] electrons with chemical potential[4] μ the probability of an eigenstate of energy E being occupied[5] is given by the Fermi factor (See Fig. 4.1)

$$n_F(\beta(E-\mu)) = \frac{1}{e^{\beta(E-\mu)}+1}. \tag{4.1}$$

At low temperature the Fermi function becomes a step function (states below the chemical potential are filled, those above the chemical potential are empty), whereas at higher temperatures the step function becomes more smeared out.

We will consider the electrons to be in a box of size $V = L^3$ and, as with our discussion in Section 2.2.1, it is easiest to imagine that

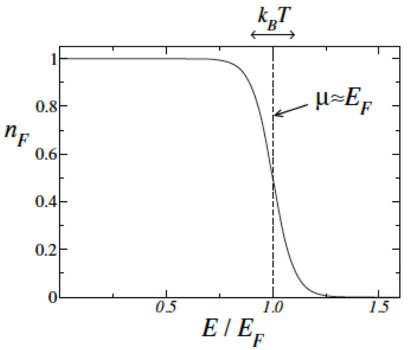


Fig. 4.1 The Fermi distribution for $k_BT \ll E_F$. The dashed line marks the chemical potential μ, which is approximately E_F. At $T = 0$ the distribution is a step, but for finite T it gets smeared over a range of energies of width a few times k_BT.

---

[1] Fermi–Dirac statistics were actually derived first by Pascual Jordan in 1925. Unfortunately, the referee of the manuscript, Max Born, misplaced it and it never got published. Many people believe that were it not for the fact that Jordan later joined the Nazi party, he might have won the Nobel Prize along with Born and Walther Bothe.

[2] Sommerfeld never won a Nobel Prize, although he was nominated for it 81 times—more than any other physicist. He was also a research advisor for more Nobel laureates than anyone else in history, including Heisenberg, Pauli, Debye, Bethe, Pauling, and Rabi.

[3] Here "free" means that they do not interact with each other, with the background crystal lattice, with impurities, or with anything else for that matter.

[4] In case you did not properly learn about chemical potential in your statistical physics course, it can be *defined* via Eq. 4.1, by saying that μ is whatever constant needs to be inserted into this equation to make it true. It can also be defined as an appropriate thermodynamical derivative such as $\mu = \partial U/\partial N|_{V,S}$ with U the total energy and N the number of particles or $\mu = \partial G/\partial N|_{T,P}$, with G the Gibbs potential. However, such a definition can be tricky if one worries about the discreteness of the particle number—since N must be an integer, the derivative may not be well defined. As a result the definition in terms of Eq. 4.1 is frequently best (i.e., we are treating μ as a Lagrange multiplier).

[5] When we say that there are a particular set of N orbitals occupied by electrons, we really mean that the overall wavefunction of the system is an antisymmetric function which can be expressed as a Slater determinant of N single electron wavefunctions. We will never need to actually write out such Slater determinant wavefunctions except in Section 23.3, which is somewhat more advanced material.

the box has periodic boundary conditions.[6] The plane wavefunctions are of the form $e^{i\mathbf{k}\cdot\mathbf{r}}$ where due to the boundary conditions $\mathbf{k}$ must take value $(2\pi/L)(n_1, n_2, n_3)$ with n_i integers. These plane waves have corresponding energies

$$\epsilon(\mathbf{k}) = \frac{\hbar^2|\mathbf{k}|^2}{2m} \tag{4.2}$$

with m the electron mass. Thus the total number of electrons in the system is given by

$$N = 2\sum_{\mathbf{k}} n_F(\beta(\epsilon(\mathbf{k})-\mu)) = 2\frac{V}{(2\pi)^3}\int \mathbf{dk}\; n_F(\beta(\epsilon(\mathbf{k})-\mu)) \tag{4.3}$$

where the prefactor of 2 accounts for the two possible spin states for each possible wavevector $\mathbf{k}$. In fact, in a metal, N will usually be given to us, and this equation will define the chemical potential as a function of temperature.

We now define a useful concept:

Definition 4.1 *The* ***Fermi energy***, E_F *is the chemical potential at temperature* $T = 0$.

This is also sometimes called the *Fermi level*. The states that are filled at $T = 0$ are sometimes called the *Fermi sea*. Frequently one also defines a *Fermi temperature* $T_F = E_F/k_B$, and also the *Fermi wavevector* k_F defined via

$$E_F = \frac{\hbar^2 k_F^2}{2m} \tag{4.4}$$

and correspondingly a *Fermi momentum* $p_F = \hbar k_F$ and a *Fermi velocity*[7]

$$v_F = \hbar k_F/m. \tag{4.5}$$

Aside: Frequently people think of the Fermi energy as the energy of the most energetic occupied electron state in system. While this is correct in the case where you are filling a continuum of states, it can also lead you to errors in cases where the energy eigenstates are discrete (see the related footnote 4 of this chapter), or more specifically when there is a gap between the most energetic occupied electron state in the system, and the least energetic unoccupied electron state. More correctly the Fermi energy, i.e., the chemical potential at $T = 0$, will be half-way between the most energetic occupied electron state, and the least energetic unoccupied electron state (see Exercise 4.6).

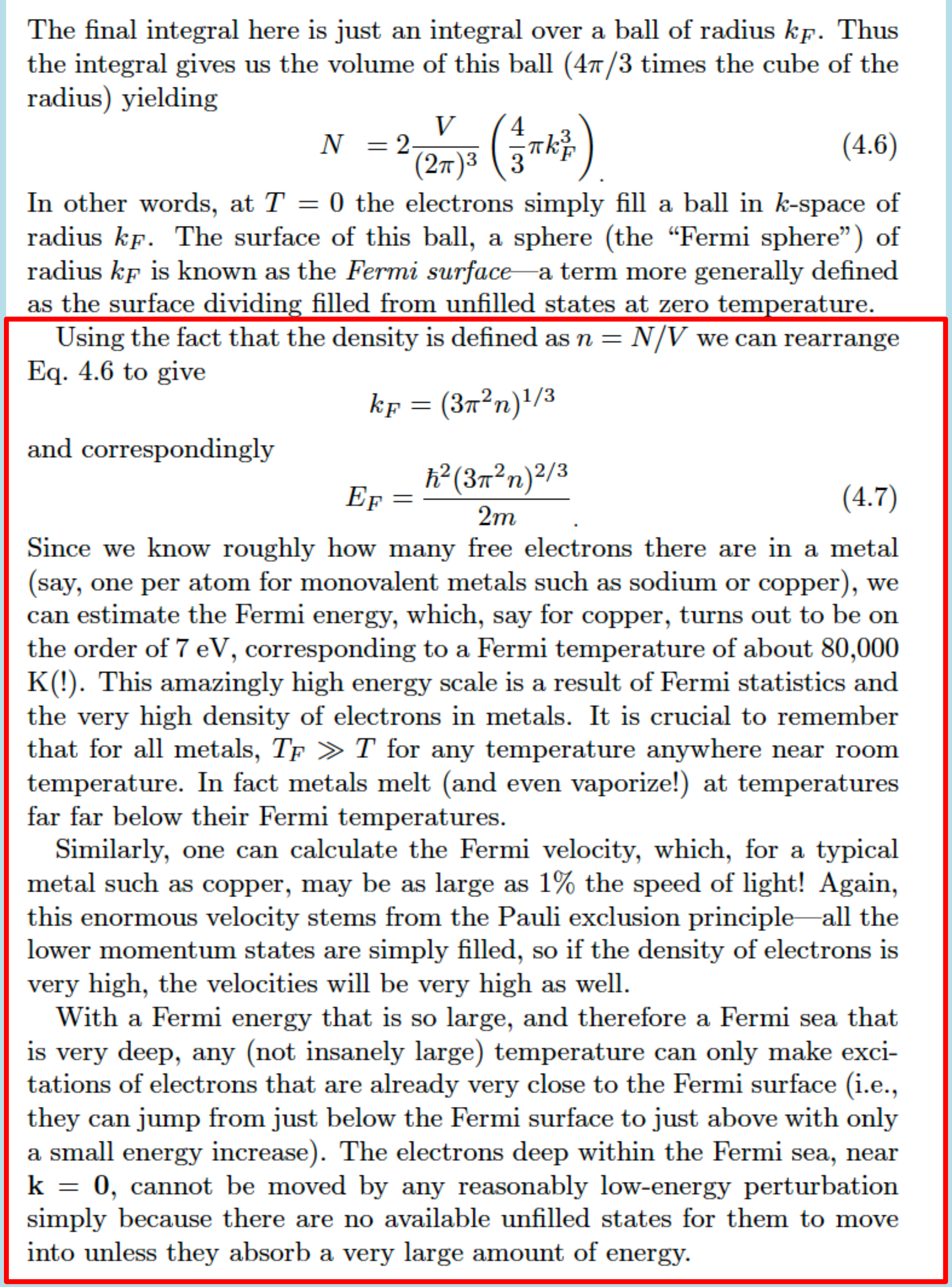
Let us now calculate the Fermi energy in a (three-dimensional) metal with N electrons in it. At $T = 0$ the Fermi function (Eq. 4.1) becomes a step function (which we write as Θ. I.e., $\Theta(x) = 1$ for $x \geqslant 0$ and $\Theta(x) = 0$ for $x < 0$), so that Eq. 4.3 becomes

$$N = 2\frac{V}{(2\pi)^3}\int \mathbf{dk}\; \Theta(E_F - \epsilon(\mathbf{k})) = 2\frac{V}{(2\pi)^3}\int^{|k|<k_F} \mathbf{dk}.$$

---

[6] As mentioned in Section 2.2.1, any properties of the bulk of the solid should be independent of the type of boundary conditions we choose. If you have doubts, you can try repeating all the calculations using hard wall boundary conditions, and you will find all the same results (It is more messy, but not too much harder!).

[7] Yes, Fermi got his name attached to many things. To help spread the credit around I've called this section "Basic Fermi–Dirac Statistics" instead of just "Basic Fermi Statistics".



The final integral here is just an integral over a ball of radius k_F. Thus the integral gives us the volume of this ball ($4\pi/3$ times the cube of the radius) yielding

$$N = 2\frac{V}{(2\pi)^3}\left(\frac{4}{3}\pi k_F^3\right). \tag{4.6}$$

In other words, at $T = 0$ the electrons simply fill a ball in k-space of radius k_F. The surface of this ball, a sphere (the "Fermi sphere") of radius k_F is known as the *Fermi surface*—a term more generally defined as the surface dividing filled from unfilled states at zero temperature.

Using the fact that the density is defined as $n = N/V$ we can rearrange Eq. 4.6 to give

$$k_F = (3\pi^2 n)^{1/3}$$

and correspondingly

$$E_F = \frac{\hbar^2(3\pi^2 n)^{2/3}}{2m}. \tag{4.7}$$

Since we know roughly how many free electrons there are in a metal (say, one per atom for monovalent metals such as sodium or copper), we can estimate the Fermi energy, which, say for copper, turns out to be on the order of 7 eV, corresponding to a Fermi temperature of about 80,000 K(!). This amazingly high energy scale is a result of Fermi statistics and the very high density of electrons in metals. It is crucial to remember that for all metals, $T_F \gg T$ for any temperature anywhere near room temperature. In fact metals melt (and even vaporize!) at temperatures far far below their Fermi temperatures.

Similarly, one can calculate the Fermi velocity, which, for a typical metal such as copper, may be as large as 1% the speed of light! Again, this enormous velocity stems from the Pauli exclusion principle—all the lower momentum states are simply filled, so if the density of electrons is very high, the velocities will be very high as well.

With a Fermi energy that is so large, and therefore a Fermi sea that is very deep, any (not insanely large) temperature can only make excitations of electrons that are already very close to the Fermi surface (i.e., they can jump from just below the Fermi surface to just above with only a small energy increase). The electrons deep within the Fermi sea, near $\mathbf{k} = \mathbf{0}$, cannot be moved by any reasonably low-energy perturbation simply because there are no available unfilled states for them to move into unless they absorb a very large amount of energy.

很值得讀。

4.2 Electronic Heat Capacity

We now turn to examine the heat capacity of electrons in a metal. Analogous to Eq. 4.3, the total energy of our system of electrons is given now by

$$\begin{aligned} E_{total} &= \frac{2V}{(2\pi)^3}\int \mathbf{dk}\,\epsilon(\mathbf{k})\,n_F(\beta(\epsilon(\mathbf{k})-\mu)) \\ &= \frac{2V}{(2\pi)^3}\int_0^\infty 4\pi k^2 dk\,\epsilon(\mathbf{k})\,n_F(\beta(\epsilon(\mathbf{k})-\mu)) \end{aligned}$$

where the chemical potential is defined as above by

$$N = \frac{2V}{(2\pi)^3}\int \mathbf{dk}\,n_F(\beta(\epsilon(\mathbf{k})-\mu)) = \frac{2V}{(2\pi)^3}\int_0^\infty 4\pi k^2 dk\;n_F(\beta(\epsilon(\mathbf{k})-\mu)).$$

(In both equations we have changed to spherical coordinates to obtain a one-dimensional integral and a factor of $4\pi k^2$ out front.)

It is convenient to replace k in this equation by the energy ϵ by using Eq. 4.2 or equivalently

$$k = \sqrt{\frac{2\epsilon m}{\hbar^2}}$$

so that

$$dk = \sqrt{\frac{m}{2\epsilon\hbar^2}}\;d\epsilon.$$

We can then rewrite these expressions as

$$\begin{aligned} E_{total} &= V\int_0^\infty d\epsilon\;\epsilon\;g(\epsilon)\;n_F(\beta(\epsilon-\mu)) && (4.8) \\ N &= V\int_0^\infty d\epsilon\;g(\epsilon)\;n_F(\beta(\epsilon-\mu)) && (4.9) \end{aligned}$$

where

$$\begin{aligned} g(\epsilon)d\epsilon &= \frac{2}{(2\pi)^3}4\pi k^2 dk = \frac{2}{(2\pi)^3}4\pi\left(\frac{2\epsilon m}{\hbar^2}\right)\sqrt{\frac{m}{2\epsilon\hbar^2}}\;d\epsilon \\ &= \frac{(2m)^{3/2}}{2\pi^2\hbar^3}\epsilon^{1/2}d\epsilon && (4.10) \end{aligned}$$

is the *density of states per unit volume.* The definition[8] of this quantity is such that $g(\epsilon)d\epsilon$ is the total number of eigenstates (including both spin states) with energies between ϵ and $\epsilon + d\epsilon$.

From Eq. 4.7 we can simply derive $(2m)^{3/2}/\hbar^3 = 3\pi^2 n/E_F^{3/2}$, thus we can simplify the density of states expression to

$$g(\epsilon) = \frac{3n}{2E_F}\left(\frac{\epsilon}{E_F}\right)^{1/2} \qquad (4.11)$$

which is a fair bit simpler. Note that the density of states has dimensions of a density (an inverse volume) divided by an energy. It is clear that this is the dimensions it must have, given Eq. 4.9 for example.

Note that the expression Eq. 4.9 should be thought of as defining the chemical potential given the number of electrons in the system and the temperature. Once the chemical potential is fixed, then Eq. 4.8 gives us the total kinetic energy of the system. Differentiating that quantity would give us the heat capacity. Unfortunately there is no way to do this analytically in all generality. However, we can use to our advantage that $T \ll T_F$ for any reasonable temperature, so that the Fermi factors n_F are close to a step function. Such an expansion was first used by Sommerfeld, but it is algebraically rather complicated[9] (see Ashcroft and Mermin Chapter 2 to see how it is done in detail). However, it is not hard to make an estimate of what such a calculation must give—which we shall now do.

When $T = 0$ the Fermi function is a step function and the chemical potential is (by definition) the Fermi energy. For small T, the step function is smeared out as we see in Fig. 4.1. Note, however, that in this smearing, the number of states that are removed from below the chemical potential is almost exactly the same as the number of states that are added above the chemical potential.[10] Thus, for small T, one does not have to move the chemical potential much from the Fermi energy in order to keep the number of particles fixed in Eq. 4.9. We conclude that $\mu \approx E_F$ for any low temperature. (In more detail we find that $\mu(T) = E_F + \mathcal{O}(T/T_F)^2$, see Ashcroft and Mermin Chapter 2.)

Thus we can focus on Eq. 4.8 with the assumption that $\mu = E_F$. At $T = 0$ let us call the kinetic energy[11] of the system $E(T = 0)$. At finite temperature, instead of a step function in Eq. 4.8 the step is smeared out as in Fig. 4.1. We see in the figure that only electrons within an energy range of roughly $k_B T$ of the Fermi surface can be excited—in general they are excited above the Fermi surface by an energy of about $k_B T$. Thus we can approximately write

$$E(T) = E(T = 0) + (\tilde{\gamma}/2)[V g(E_F)(k_B T)](k_B T) + \dots .$$

Here $V g(E_F)$ is the density of states near the Fermi surface (recall g is the density of states per unit volume), so the number of particles close enough to the Fermi surface to be excited is $V g(E_F)(k_B T)$, and the final factor of $(k_B T)$ is roughly the amount of energy that each one gets excited by. Here $\tilde{\gamma}$ is some constant which we cannot get right by such an approximate argument (but it can be derived more carefully, and it turns out that $\tilde{\gamma} = \pi^2/3$, see Ashcroft and Mermin).

We can then derive the heat capacity

$$C = \partial E/\partial T = \tilde{\gamma} k_B g(E_F) k_B T V$$

which then using Eq. 4.11 we can rewrite as

$$C = \tilde{\gamma}\left(\frac{3Nk_B}{2}\right)\left(\frac{T}{T_F}\right). \tag{4.12}$$

The first term in brackets is just the classical result for the heat capacity of a gas, but the final factor T/T_F is tiny (0.01 or smaller!). This is the above promised linear T term in the heat capacity of electrons (see Fig. 2.5), which is far smaller than one would get for a classical gas.

This Sommerfeld prediction for the electronic (linear T) contribution to the heat capacity of a metal is typically not too far from being correct (see Table 4.1). A few metals, however, have specific heats that deviate from this prediction by a factor of 10 or more. Note that there are other measurements that indicate that these errors are associated with the electron mass being somehow changed in the metal. We will discover the reason for these deviations later when we study band theory (mainly in Chapter 17).

Table 4.1 Low-temperature heat capacity coefficient for some metals. All of these metals have heat capacities of the form $C = \gamma T + \alpha T^3$ at low temperature. This table gives the measured experimental (exp) value and the Sommerfeld theoretical (th) predictions for the coefficient γ in units of 10^{-4} J/(mol-K).

Material	γ_{exp}	γ_{th}
Lithium (Li)	18	7.4
Sodium (Na)	15	11
Potassium (K)	20	17
Copper (Cu)	7	5.0
Silver (Ag)	7	6.4
Beryllium (Be)	2	2.5
Bismuth (Bi)	1	5.0
Manganese (Mn)	170	5.2

The theoretical value is obtained by setting the electron density equal to the atomic density times the valence (number of free electrons per atom), then calculating the Fermi temperature from the density and using Eq. 4.12. Note that Mn has multiple possible valence states. In the theoretical calculation we assume valence of one which gives the largest possible predicted value of γ_{th}.

---

[10] Since the Fermi function has a precise symmetry around μ given by $n_F(\beta(E - \mu)) = 1 - n_F(\beta(\mu - E))$, this equivalence of states removed from below the chemical potential and states inserted above would be an exact statement if the density of states in Eq. 4.9 were independent of energy.

[11] In fact $E(T = 0) = (3/5)NE_F$, which is not too hard to show. See Exercise 4.1.

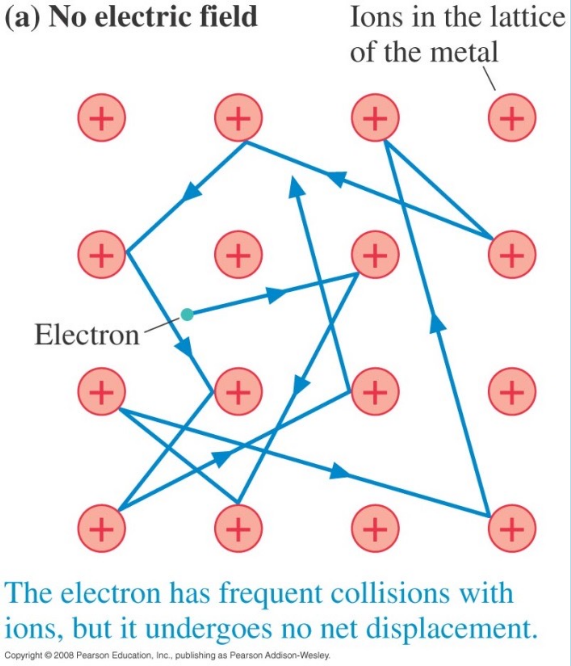
電場對電子產生一加速度： $a = \frac{F}{m} = \frac{eE}{m}$

這是等加速度運動，電子速度一直增加，直到與離子碰撞後大致歸零。

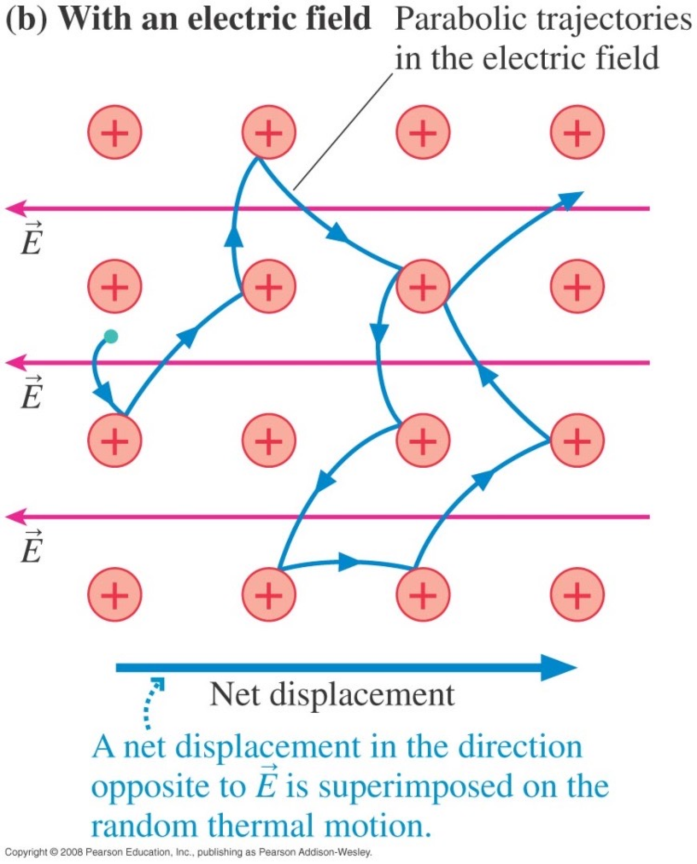
我們可以兩次碰撞間，電子的平均速度，來估計電子漂移的平均速度。

平均漂移速度 $v_d = a\tau = \frac{e\tau}{m}E$ τ 是兩次碰撞間的平均間隔時間

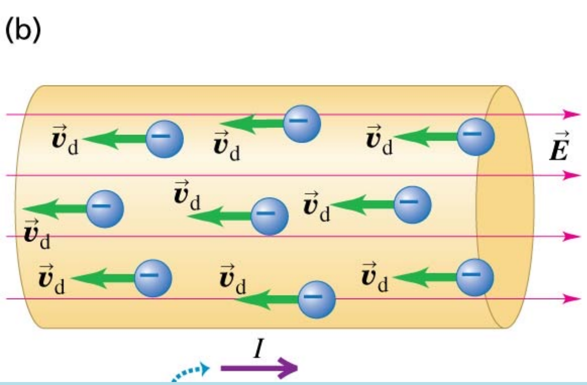
平均漂移速度與電場成正比。



The electron has frequent collisions with ions, but it undergoes no net displacement.

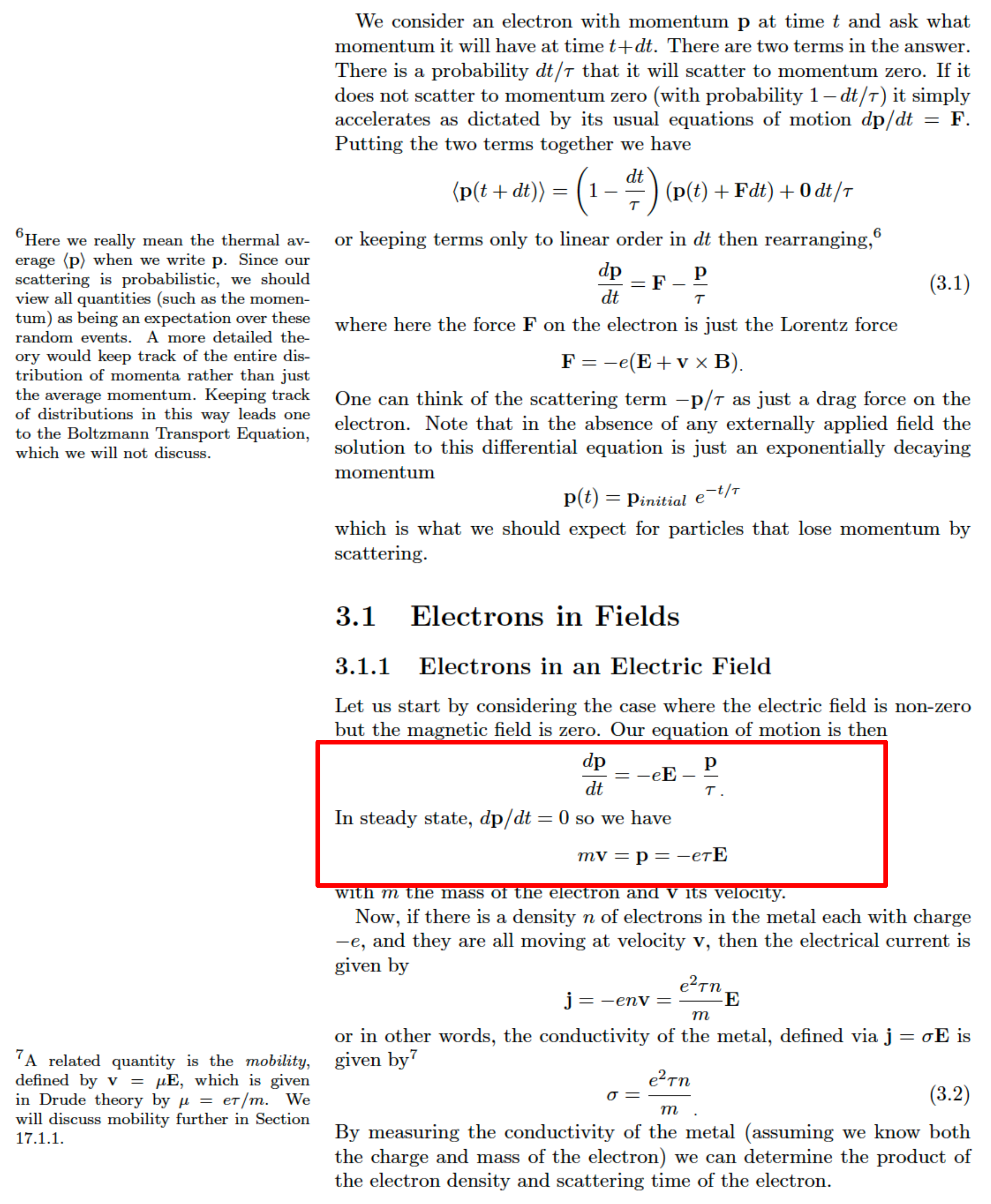


A net displacement in the direction opposite to $\vec{E}$ is superimposed on the random thermal motion.



比較進化的推導：

$$v_d = \frac{e\tau}{m} E$$



We consider an electron with momentum $\mathbf{p}$ at time t and ask what momentum it will have at time $t+dt$. There are two terms in the answer. There is a probability dt/τ that it will scatter to momentum zero. If it does not scatter to momentum zero (with probability $1-dt/\tau$) it simply accelerates as dictated by its usual equations of motion $d\mathbf{p}/dt = \mathbf{F}$. Putting the two terms together we have

$$\langle \mathbf{p}(t+dt)\rangle = \left(1 - \frac{dt}{\tau}\right)(\mathbf{p}(t) + \mathbf{F}dt) + \mathbf{0}\, dt/\tau$$

or keeping terms only to linear order in dt then rearranging,[6]

$$\frac{d\mathbf{p}}{dt} = \mathbf{F} - \frac{\mathbf{p}}{\tau} \qquad (3.1)$$

where here the force $\mathbf{F}$ on the electron is just the Lorentz force

$$\mathbf{F} = -e(\mathbf{E} + \mathbf{v}\times\mathbf{B}).$$

One can think of the scattering term $-\mathbf{p}/\tau$ as just a drag force on the electron. Note that in the absence of any externally applied field the solution to this differential equation is just an exponentially decaying momentum

$$\mathbf{p}(t) = \mathbf{p}_{initial}\; e^{-t/\tau}$$

which is what we should expect for particles that lose momentum by scattering.

3.1 Electrons in Fields

3.1.1 Electrons in an Electric Field

Let us start by considering the case where the electric field is non-zero but the magnetic field is zero. Our equation of motion is then

$$\frac{d\mathbf{p}}{dt} = -e\mathbf{E} - \frac{\mathbf{p}}{\tau}.$$

In steady state, $d\mathbf{p}/dt = 0$ so we have

$$m\mathbf{v} = \mathbf{p} = -e\tau\mathbf{E}$$

with m the mass of the electron and $\mathbf{v}$ its velocity.

Now, if there is a density n of electrons in the metal each with charge $-e$, and they are all moving at velocity $\mathbf{v}$, then the electrical current is given by

$$\mathbf{j} = -en\mathbf{v} = \frac{e^2\tau n}{m}\mathbf{E}$$

or in other words, the conductivity of the metal, defined via $\mathbf{j} = \sigma\mathbf{E}$ is given by[7]

$$\sigma = \frac{e^2\tau n}{m}. \qquad (3.2)$$

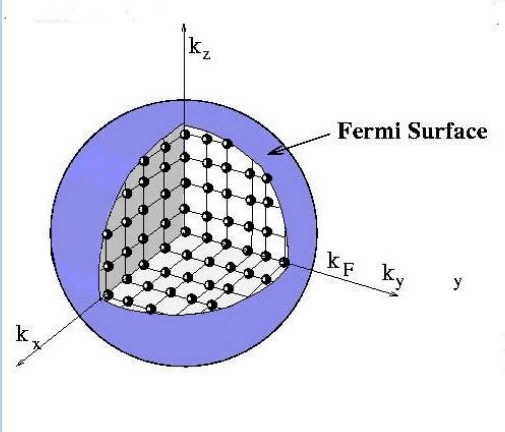
By measuring the conductivity of the metal (assuming we know both the charge and mass of the electron) we can determine the product of the electron density and scattering time of the electron.

[6] Here we really mean the thermal average $\langle\mathbf{p}\rangle$ when we write $\mathbf{p}$. Since our scattering is probabilistic, we should view all quantities (such as the momentum) as being an expectation over these random events. A more detailed theory would keep track of the entire distribution of momenta rather than just the average momentum. Keeping track of distributions in this way leads one to the Boltzmann Transport Equation, which we will not discuss.

[7] A related quantity is the *mobility*, defined by $\mathbf{v} = \mu\mathbf{E}$, which is given in Drude theory by $\mu = e\tau/m$. We will discuss mobility further in Section 17.1.1.

有電子佔據的態就在一個球內！此球面是能量最高的邊界，就稱為費米面！

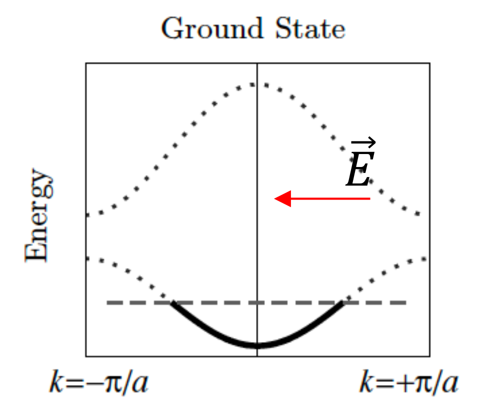
費米面在常數電場下會沿電場反方向定速移動。

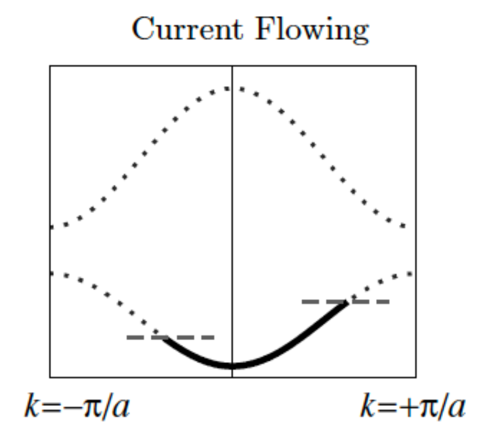


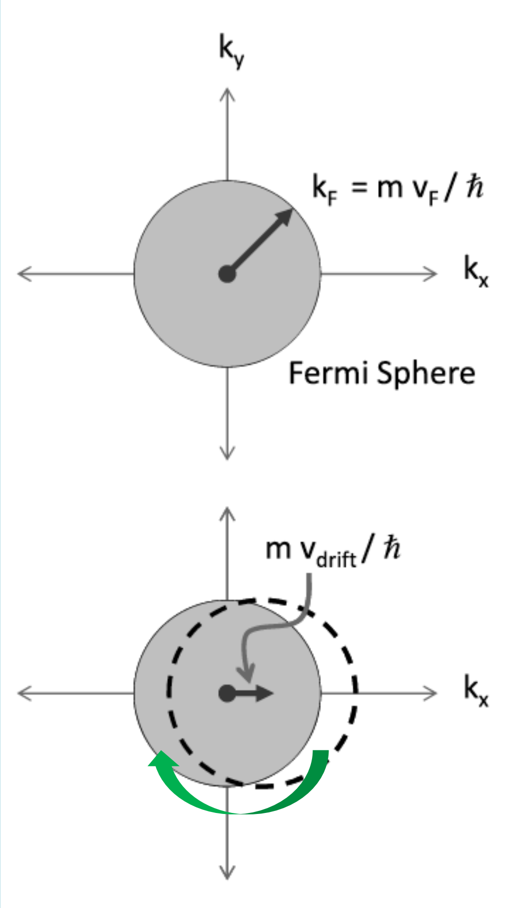
$$\hbar\frac{dk}{dt} = eE - \frac{\hbar k}{\tau}$$

$\hbar k_d = eE\tau$ 達到穩定的飄移

$$v_d = \frac{\hbar k_d}{m} = \frac{e\tau}{m}E$$







同時，右邊能量超越原本費米面的電子，可以與離子散射，回到能量較低的狀態。

兩個過程彼此抵消時，高斯面就會停在該處，此時的平均$\hbar k_d = eE\tau$。

平均速度v_d就維持向右大概不變，