

# **Quantum Mechanics**

# Identical Particles

For a *single* particle,  $\Psi(\mathbf{r}, t)$  is a function of the spatial coordinates,  $\mathbf{r}$ , and the time,  $t$  (we'll ignore spin, for the moment). The state of a *two*-particle system is a function of the coordinates of particle one ( $\mathbf{r}_1$ ), the coordinates of particle two ( $\mathbf{r}_2$ ), and the time:

$$\Psi(\mathbf{r}_1, \mathbf{r}_2, t).$$

Its time evolution is determined (as always) by the Schrödinger equation:

$$i\hbar \frac{\partial \Psi}{\partial t} = H\Psi,$$

where  $H$  is the Hamiltonian for the whole system:

$$H = -\frac{\hbar^2}{2m_1} \nabla_1^2 - \frac{\hbar^2}{2m_2} \nabla_2^2 + V(\mathbf{r}_1, \mathbf{r}_2, t)$$

(the subscript on  $\nabla$  indicates differentiation with respect to the coordinates of particle 1 or particle 2, as the case may be). The statistical interpretation carries over in the obvious way:

$$|\Psi(\mathbf{r}_1, \mathbf{r}_2, t)|^2 d^3\mathbf{r}_1 d^3\mathbf{r}_2$$

is the probability of finding particle 1 in the volume  $d^3\mathbf{r}_1$  *and* particle 2 in the volume  $d^3\mathbf{r}_2$ ; evidently  $\Psi$  must be normalized in such a way that

$$\int |\Psi(\mathbf{r}_1, \mathbf{r}_2, t)|^2 d^3\mathbf{r}_1 d^3\mathbf{r}_2 = 1.$$

For time-independent potentials, we obtain a complete set of solutions by separation of variables:

$$\Psi(\mathbf{r}_1, \mathbf{r}_2, t) = \psi(\mathbf{r}_1, \mathbf{r}_2)e^{-iEt/\hbar},$$

where the spatial wave function ( $\psi$ ) satisfies the time-independent Schrödinger equation:

$$-\frac{\hbar^2}{2m_1} \nabla_1^2 \psi - \frac{\hbar^2}{2m_2} \nabla_2^2 \psi + V\psi = E\psi,$$

and  $E$  is the total energy of the system.

Suppose particle 1 is in the (one-particle) state  $\psi_a(\mathbf{r})$ , and particle 2 is in the state  $\psi_b(\mathbf{r})$ . (Remember: I'm ignoring spin, for the moment.) In that case  $\psi(\mathbf{r}_1, \mathbf{r}_2)$  is a simple *product*:

$$\psi(\mathbf{r}_1, \mathbf{r}_2) = \psi_a(\mathbf{r}_1)\psi_b(\mathbf{r}_2).$$

Of course, this assumes that we can tell the particles apart—otherwise it wouldn't make any sense to claim that number 1 is in state  $\psi_a$  and number 2 is in state  $\psi_b$ ; all we could say is that *one* of them is in the state  $\psi_a$  and the other is in state  $\psi_b$ , but we wouldn't know which is which. If we were talking *classical* mechanics this would be a silly objection:

All electrons are “identical”. There is no way label them distinctively!

# Identical Particles

Quantum mechanics neatly accommodates the existence of particles that are *indistinguishable in principle*: We simply construct a wave function that is *non-committal* as to which particle is in which state. There are actually *two* ways to do it:

$$\psi_{\pm}(\mathbf{r}_1, \mathbf{r}_2) = A[\psi_a(\mathbf{r}_1)\psi_b(\mathbf{r}_2) \pm \psi_b(\mathbf{r}_1)\psi_a(\mathbf{r}_2)].$$

Thus the theory admits two kinds of identical particles: **bosons**, for which we use the plus sign, and **fermions**, for which we use the minus sign. Photons and mesons are bosons; protons and electrons are fermions. It so happens that

all particles with *integer* spin are bosons, and  
all particles with *half integer* spin are fermions.

This connection between **spin and statistics** (as we shall see, bosons and fermions have quite different statistical properties) can be *proved* in *relativistic* quantum mechanics; in the nonrelativistic theory it is taken as an axiom.

It follows, in particular, that *two identical fermions* (for example, two electrons) *cannot occupy the same state*. For if  $\psi_a = \psi_b$ , then

$$\psi_{-}(\mathbf{r}_1, \mathbf{r}_2) = A[\psi_a(\mathbf{r}_1)\psi_a(\mathbf{r}_2) - \psi_a(\mathbf{r}_1)\psi_a(\mathbf{r}_2)] = 0,$$

and we are left with no wave function at all. This is the famous **Pauli exclusion principle**. It is not (as you may have been led to believe) a weird ad hoc assumption applying only to electrons, but rather a consequence of the rules for constructing two-particle wave functions, applying to *all* identical fermions.

Let us define the **exchange operator**,  $P$ , which interchanges the two particles:

$$Pf(\mathbf{r}_1, \mathbf{r}_2) = f(\mathbf{r}_2, \mathbf{r}_1).$$

Clearly,  $P^2 = 1$ , and it follows (prove it for yourself) that the eigenvalues of  $P$  are  $\pm 1$ . Now, if the two particles are identical, the Hamiltonian must treat them the same:  $m_1 = m_2$  and  $V(\mathbf{r}_1, \mathbf{r}_2) = V(\mathbf{r}_2, \mathbf{r}_1)$ . It follows that  $P$  and  $H$  are compatible observables,

$$[P, H] = 0,$$

and hence we can find a complete set of functions that are simultaneous eigenstates of both. That is to say, we can find solutions to the Schrödinger equation that are either symmetric (eigenvalue  $+1$ ) or antisymmetric (eigenvalue  $-1$ ) under exchange:

$$\psi(\mathbf{r}_1, \mathbf{r}_2) = \pm \psi(\mathbf{r}_2, \mathbf{r}_1).$$

Moreover, if a system starts out in such a state, it will remain in such a state. The *new* law (I'll call it the **symmetrization requirement**) is that for identical particles the wave function is not merely *allowed*, but *required* to satisfy with the plus sign for bosons, and the minus sign for fermions.

# Identical Particles

**Example 5.1** Suppose we have two noninteracting—they pass right through one another . . . never mind how you would set this up in practice!—particles, both of mass  $m$ , in the infinite square well

The one-particle states are

$$\psi_n(x) = \sqrt{\frac{2}{a}} \sin\left(\frac{n\pi}{a}x\right), \quad E_n = n^2 K$$

(where  $K \equiv \pi^2 \hbar^2 / 2ma^2$ , for convenience). If the particles are *distinguishable*, with #1 in state  $n_1$  and #2 in state  $n_2$ , the composite wave function is a simple product:

$$\psi_{n_1 n_2}(x_1, x_2) = \psi_{n_1}(x_1)\psi_{n_2}(x_2), \quad E_{n_1 n_2} = (n_1^2 + n_2^2)K.$$

For example, the ground state is

$$\psi_{11} = \frac{2}{a} \sin(\pi x_1/a) \sin(\pi x_2/a), \quad E_{11} = 2K;$$

the first excited state is doubly degenerate:

$$\psi_{12} = \frac{2}{a} \sin(\pi x_1/a) \sin(2\pi x_2/a), \quad E_{12} = 5K,$$

$$\psi_{21} = \frac{2}{a} \sin(2\pi x_1/a) \sin(\pi x_2/a), \quad E_{21} = 5K;$$

and so on. If the two particles are identical *bosons*, the ground state is unchanged, but the first excited state is *nondegenerate*:

$$\frac{\sqrt{2}}{a} [\sin(\pi x_1/a) \sin(2\pi x_2/a) + \sin(2\pi x_1/a) \sin(\pi x_2/a)]$$

(still with energy  $5K$ ). And if the particles are identical *fermions*, there is *no* state with energy  $2K$ ; the ground state is

$$\frac{\sqrt{2}}{a} [\sin(\pi x_1/a) \sin(2\pi x_2/a) - \sin(2\pi x_1/a) \sin(\pi x_2/a)],$$

and its energy is  $5K$ .

Suppose one particle is in state  $\psi_a(x)$ , and the other is in state  $\psi_b(x)$ , and these two states are orthogonal and normalized.

If the two particles are distinguishable, and number 1 is the one in state  $\psi_a$ , then the combined wave function is

$$\psi(x_1, x_2) = \psi_a(x_1)\psi_b(x_2);$$

if they are identical bosons, the composite wave function is

$$\psi_+(x_1, x_2) = \frac{1}{\sqrt{2}} [\psi_a(x_1)\psi_b(x_2) + \psi_b(x_1)\psi_a(x_2)];$$

and if they are identical fermions, it is

$$\psi_-(x_1, x_2) = \frac{1}{\sqrt{2}} [\psi_a(x_1)\psi_b(x_2) - \psi_b(x_1)\psi_a(x_2)].$$

Let's calculate the expectation value of the square of the separation distance between the two particles,

$$\langle (x_1 - x_2)^2 \rangle = \langle x_1^2 \rangle + \langle x_2^2 \rangle - 2\langle x_1 x_2 \rangle,$$

# Identical Particles

$$\langle (x_1 - x_2)^2 \rangle = \langle x_1^2 \rangle + \langle x_2^2 \rangle - 2\langle x_1 x_2 \rangle,$$

## Distinguishable Particles

$$\langle x_1^2 \rangle = \int x_1^2 |\psi_a(x_1)|^2 dx_1 \int |\psi_b(x_2)|^2 dx_2 = \langle x^2 \rangle_a$$

(the expectation value of  $x^2$  in the one-particle state  $\psi_a$ ),

$$\langle x_2^2 \rangle = \int |\psi_a(x_1)|^2 dx_1 \int x_2^2 |\psi_b(x_2)|^2 dx_2 = \langle x^2 \rangle_b,$$

and

$$\langle x_1 x_2 \rangle = \int x_1 |\psi_a(x_1)|^2 dx_1 \int x_2 |\psi_b(x_2)|^2 dx_2 = \langle x \rangle_a \langle x \rangle_b.$$

In this case, then,

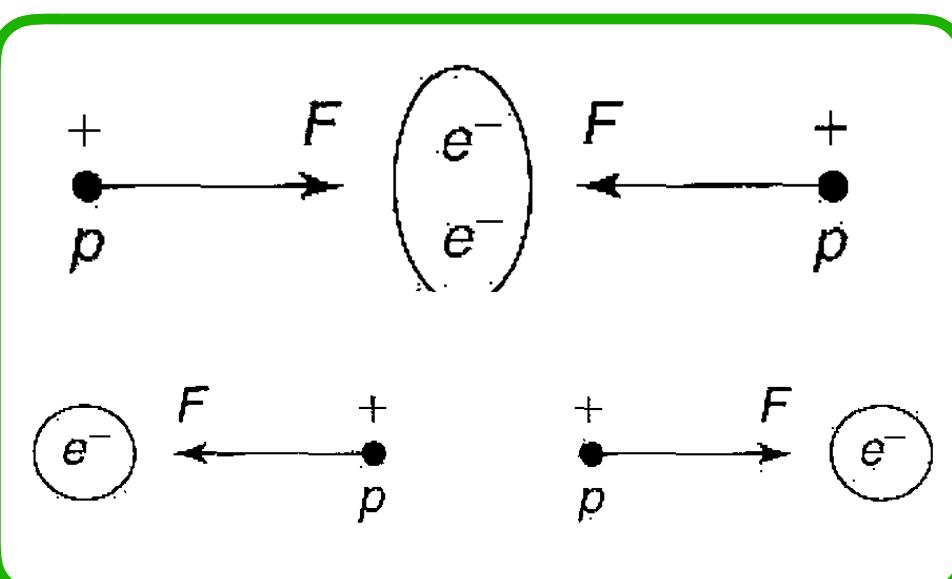
$$\langle (x_1 - x_2)^2 \rangle_d = \langle x^2 \rangle_a + \langle x^2 \rangle_b - 2\langle x \rangle_a \langle x \rangle_b.$$

(Incidentally, the answer would, of course, be the same if particle 1 had been in state  $\psi_b$ , and particle 2 in state  $\psi_a$ .)

## Identical Particles

$$\psi_+(x_1, x_2) = \frac{1}{\sqrt{2}} [\psi_a(x_1)\psi_b(x_2) + \psi_b(x_1)\psi_a(x_2)];$$

$$\psi_-(x_1, x_2) = \frac{1}{\sqrt{2}} [\psi_a(x_1)\psi_b(x_2) - \psi_b(x_1)\psi_a(x_2)].$$



## Identical Particles

$$\begin{aligned} \langle x_1^2 \rangle &= \frac{1}{2} \left[ \int x_1^2 |\psi_a(x_1)|^2 dx_1 \int |\psi_b(x_2)|^2 dx_2 + \int x_1^2 |\psi_b(x_1)|^2 dx_1 \int |\psi_a(x_2)|^2 dx_2 \right. \\ &\quad \left. \pm \int x_1^2 \psi_a(x_1)^* \psi_b(x_1) dx_1 \int \psi_b(x_2)^* \psi_a(x_2) dx_2 \pm \int x_1^2 \psi_b(x_1)^* \psi_a(x_1) dx_1 \int \psi_a(x_2)^* \psi_b(x_2) dx_2 \right] \\ &= \frac{1}{2} [\langle x^2 \rangle_a + \langle x^2 \rangle_b \pm 0 \pm 0] = \frac{1}{2} (\langle x^2 \rangle_a + \langle x^2 \rangle_b). \end{aligned}$$

Similarly,  $\langle x_2^2 \rangle = \frac{1}{2} (\langle x^2 \rangle_b + \langle x^2 \rangle_a)$ . (Naturally,  $\langle x_2^2 \rangle = \langle x_1^2 \rangle$ , since you can't tell them apart.)

$$\begin{aligned} \langle x_1 x_2 \rangle &= \frac{1}{2} \left[ \int x_1 |\psi_a(x_1)|^2 dx_1 \int x_2 |\psi_b(x_2)|^2 dx_2 + \int x_1 |\psi_b(x_1)|^2 dx_1 \int x_2 |\psi_a(x_2)|^2 dx_2 \right. \\ &\quad \left. \pm \int x_1 \psi_a(x_1)^* \psi_b(x_1) dx_1 \int x_2 \psi_b(x_2)^* \psi_a(x_2) dx_2 \right. \\ &\quad \left. \pm \int x_1 \psi_b(x_1)^* \psi_a(x_1) dx_1 \int x_2 \psi_a(x_2)^* \psi_b(x_2) dx_2 \right] \\ &= \frac{1}{2} (\langle x \rangle_a \langle x \rangle_b + \langle x \rangle_b \langle x \rangle_a \pm \langle x \rangle_{ab} \langle x \rangle_{ba} \pm \langle x \rangle_{ba} \langle x \rangle_{ab}) \\ &= \langle x \rangle_a \langle x \rangle_b \pm |\langle x \rangle_{ab}|^2, \end{aligned}$$

where  $\langle x \rangle_{ab} \equiv \int x \psi_a(x)^* \psi_b(x) dx$ .

$$\langle (x_1 - x_2)^2 \rangle_{\pm} = \langle x^2 \rangle_a + \langle x^2 \rangle_b - 2\langle x \rangle_a \langle x \rangle_b \mp 2|\langle x \rangle_{ab}|^2.$$

## Difference

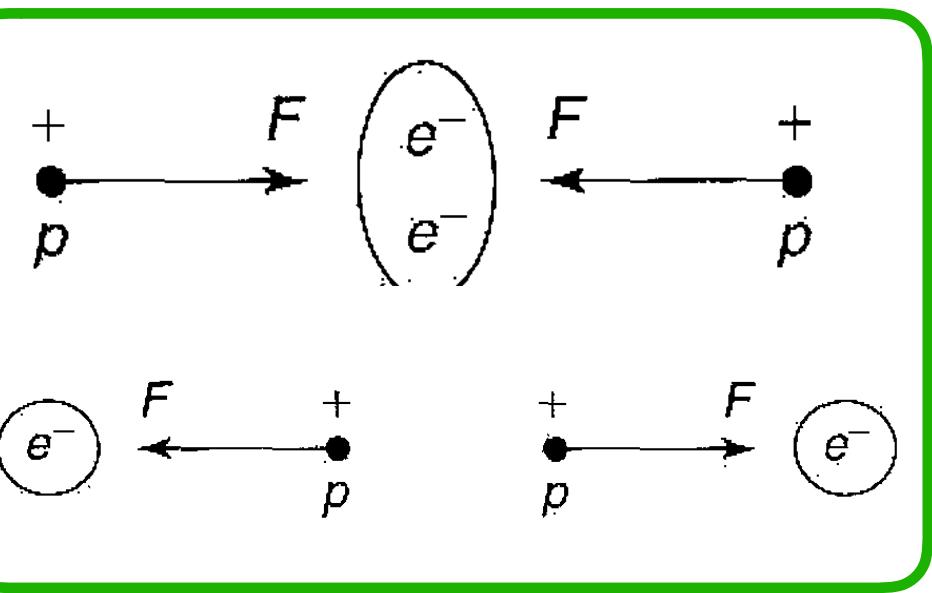
$$\langle (\Delta x)^2 \rangle_{\pm} = \langle (\Delta x)^2 \rangle_d \mp 2|\langle x \rangle_{ab}|^2.$$

# Identical Particles

## Identical Particles

$$\psi_+(x_1, x_2) = \frac{1}{\sqrt{2}} [\psi_a(x_1)\psi_b(x_2) + \psi_b(x_1)\psi_a(x_2)];$$

$$\psi_-(x_1, x_2) = \frac{1}{\sqrt{2}} [\psi_a(x_1)\psi_b(x_2) - \psi_b(x_1)\psi_a(x_2)].$$



The *interesting* case is when there *is* some overlap of the wave functions. The system behaves as though there were a “force of attraction” between identical bosons, pulling them closer together, and a “force of repulsion” between identical fermions, pushing them apart (remember that we are for the moment ignoring spin). We call it an **exchange force**, although it’s not really a force at all—no physical agency is pushing on the particles; rather, it is a purely *geometrical* consequence of the symmetrization requirement. It is also a strictly quantum mechanical phenomenon, with no classical counterpart. Nevertheless, it has profound consequences. Consider, for example, the hydrogen molecule ( $H_2$ ).

Unfortunately, electrons *aren’t* bosons, they’re fermions, and this means that the concentration of negative charge should actually be shifted to the wings tearing the molecule apart!

But wait! We have been ignoring *spin*. The *complete* state of the electron includes not only its position wave function, but also a spinor, describing the orientation of its spin:

$$\psi(\mathbf{r})\chi(\mathbf{s}).$$

When we put together the two-electron state, it is the *whole works*, not just the spatial part, that has to be antisymmetric with respect to exchange. Now, the singlet combination is antisymmetric (and hence would have to be joined with a *symmetric* spatial function), whereas the three triplet states are all symmetric (and would require an *antisymmetric* spatial function). Evidently, then, the singlet state should lead to *bonding*, and the triplet to *anti bonding*. Sure enough, the chemists tell us that covalent bonding requires the two electrons to occupy the singlet state, with total spin zero.

## Atoms

A neutral atom, of atomic number  $Z$ , consists of a heavy nucleus, with electric charge  $Ze$ , surrounded by  $Z$  electrons (mass  $m$  and charge  $-e$ ). The Hamiltonian for this system is

$$H = \sum_{j=1}^Z \left\{ -\frac{\hbar^2}{2m} \nabla_j^2 - \left( \frac{1}{4\pi\epsilon_0} \right) \frac{Ze^2}{r_j} \right\} + \frac{1}{2} \left( \frac{1}{4\pi\epsilon_0} \right) \sum_{j \neq k}^Z \frac{e^2}{|\mathbf{r}_j - \mathbf{r}_k|}.$$

The problem is to solve Schrödinger’s equation,  $H\psi = E\psi$ , for the wave function  $\psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_Z)$ . Because electrons are identical fermions, however, not all solutions are acceptable: only those for which the complete state (position and spin),

$$\psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_Z)\chi(\mathbf{s}_1, \mathbf{s}_2, \dots, \mathbf{s}_Z),$$

is antisymmetric with respect to interchange of any two electrons. In particular, no two electrons can occupy the *same* state.

Reading task: Read about *He & the Periodic Table*

# Solids

In the solid state, a few of the loosely bound outermost **valence** electrons in each atom become detached, and roam around throughout the material, no longer subject only to the Coulomb field of a specific “parent” nucleus, but rather to the combined potential of the entire crystal lattice.

## Free Electron Gas

Suppose the object in question is a rectangular solid, with dimensions  $l_x$ ,  $l_y$ ,  $l_z$ , and imagine that an electron inside experiences no forces at all, except at the impenetrable walls:

$$V(x, y, z) = \begin{cases} 0, & \text{if } 0 < x < l_x, \quad 0 < y < l_y, \text{ and } 0 < z < l_z; \\ \infty, & \text{otherwise.} \end{cases}$$

The Schrödinger equation,

$$-\frac{\hbar^2}{2m} \nabla^2 \psi = E\psi,$$

separates, in cartesian coordinates:  $\psi(x, y, z) = X(x)Y(y)Z(z)$ , with

$$-\frac{\hbar^2}{2m} \frac{d^2X}{dx^2} = E_x X; \quad -\frac{\hbar^2}{2m} \frac{d^2Y}{dy^2} = E_y Y; \quad -\frac{\hbar^2}{2m} \frac{d^2Z}{dz^2} = E_z Z,$$

and  $E = E_x + E_y + E_z$ . Letting

$$k_x \equiv \frac{\sqrt{2mE_x}}{\hbar}, \quad k_y \equiv \frac{\sqrt{2mE_y}}{\hbar}, \quad k_z \equiv \frac{\sqrt{2mE_z}}{\hbar},$$

we obtain the general solutions

$$X(x) = A_x \sin(k_x x) + B_x \cos(k_x x), \quad Y(y) = A_y \sin(k_y y) + B_y \cos(k_y y), \\ Z(z) = A_z \sin(k_z z) + B_z \cos(k_z z).$$

The boundary conditions require that  $X(0) = Y(0) = Z(0) = 0$ , so  $B_x = B_y = B_z = 0$ , and  $X(l_x) = Y(l_y) = Z(l_z) = 0$ , so that

$$k_x l_x = n_x \pi, \quad k_y l_y = n_y \pi, \quad k_z l_z = n_z \pi,$$

where each  $n$  is a positive integer:

$$n_x = 1, 2, 3, \dots, \quad n_y = 1, 2, 3, \dots, \quad n_z = 1, 2, 3, \dots.$$

The (normalized) wave functions are

$$\psi_{n_x n_y n_z} = \sqrt{\frac{8}{l_x l_y l_z}} \sin\left(\frac{n_x \pi}{l_x} x\right) \sin\left(\frac{n_y \pi}{l_y} y\right) \sin\left(\frac{n_z \pi}{l_z} z\right),$$

and the allowed energies are

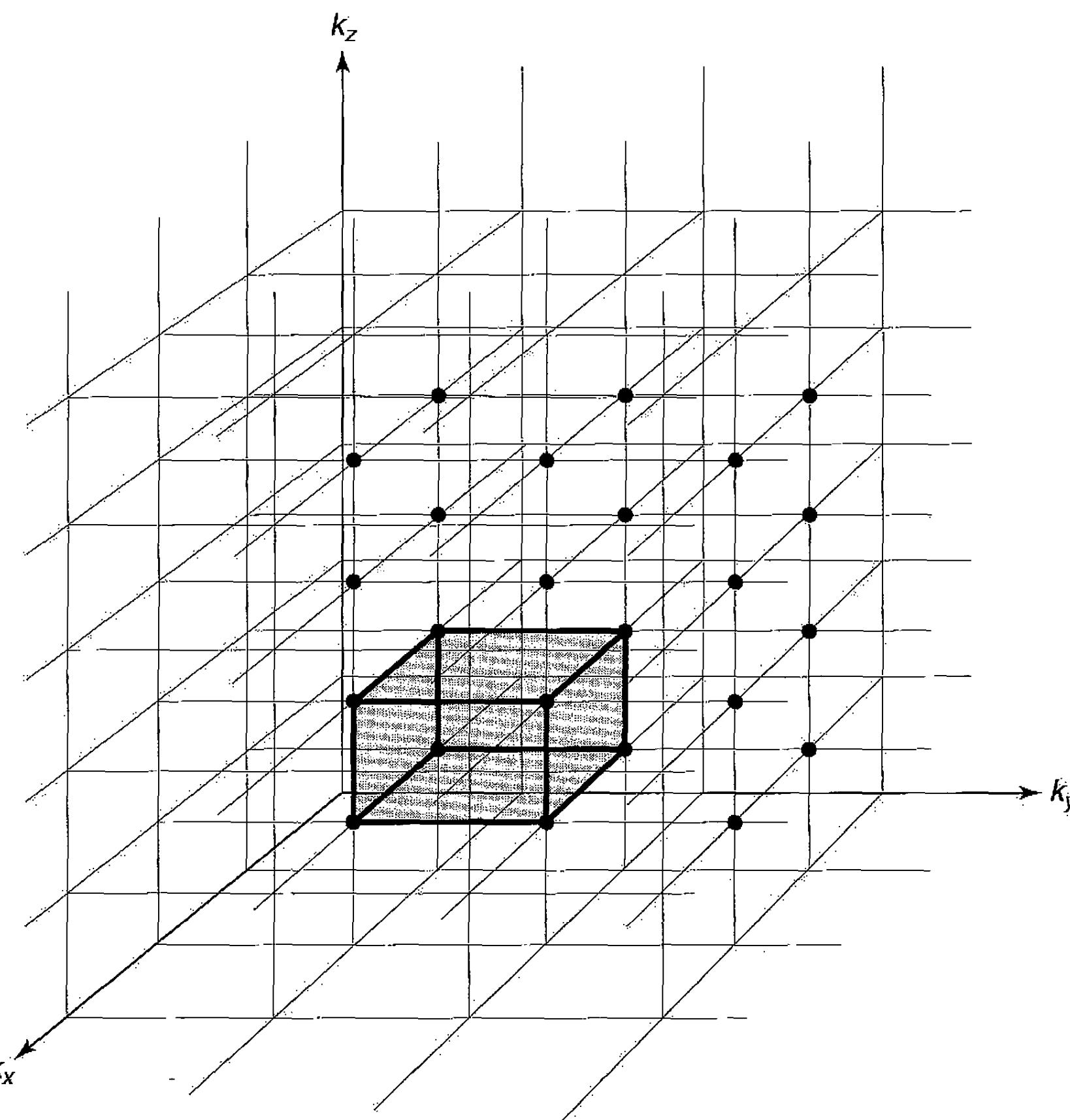
$$E_{n_x n_y n_z} = \frac{\hbar^2 \pi^2}{2m} \left( \frac{n_x^2}{l_x^2} + \frac{n_y^2}{l_y^2} + \frac{n_z^2}{l_z^2} \right) = \frac{\hbar^2 k^2}{2m},$$

where  $k$  is the magnitude of the **wave vector**,  $\mathbf{k} \equiv (k_x, k_y, k_z)$ .

# Solids

## Free Electron Gas

If you imagine a three-dimensional space, with axes  $k_x$ ,  $k_y$ ,  $k_z$ , and planes drawn in at  $k_x = (\pi/l_x)$ ,  $(2\pi/l_x)$ ,  $(3\pi/l_x)$ , ..., at  $k_y = (\pi/l_y)$ ,  $(2\pi/l_y)$ ,  $(3\pi/l_y)$ , ..., and at  $k_z = (\pi/l_z)$ ,  $(2\pi/l_z)$ ,  $(3\pi/l_z)$ , ..., each intersection point represents a distinct (one-particle) stationary state



Each block in this grid, and hence also each state, occupies a volume

$$\frac{\pi^3}{l_x l_y l_z} = \frac{\pi^3}{V}$$

of “ $k$ -space,” where  $V = l_x l_y l_z$  is the volume of the object itself. Suppose our sample contains  $N$  atoms, and each atom contributes  $q$  free electrons. (In practice,  $N$  will be enormous—on the order of Avogadro’s number, for an object of macroscopic size—whereas  $q$  is a small number—1 or 2, typically.) If electrons were bosons (or distinguishable particles), they would all settle down to the ground state,  $\psi_{111}$ . But electrons are in fact identical *fermions*, subject to the Pauli exclusion principle, so only two of them can occupy any given state. They will fill up one octant of a *sphere* in  $k$ -space, whose radius,  $k_F$ , is determined by the fact that each pair of electrons requires a volume  $\pi^3/V$

$$\frac{1}{8} \left( \frac{4}{3} \pi k_F^3 \right) = \frac{Nq}{2} \left( \frac{\pi^3}{V} \right).$$

$$\text{Thus } k_F = (3\rho\pi^2)^{1/3}, \text{ where } \rho \equiv \frac{Nq}{V}$$

is the *free electron density* (the number of free electrons per unit volume).

The boundary separating occupied and unoccupied states, in  $k$ -space, is called the **Fermi surface** (hence the subscript  $F$ ). The corresponding energy is called the **Fermi energy**,  $E_F$ ; for a free electron gas,

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

# Solids

## Free Electron Gas

The *total* energy of the electron gas can be calculated as follows: A shell of thickness  $dk$  contains a volume

$$\frac{1}{8}(4\pi k^2) dk,$$

so the number of electron states in the shell is

$$\frac{2[(1/2)\pi k^2 dk]}{(\pi^3/V)} = \frac{V}{\pi^2} k^2 dk.$$

Each of these states carries an energy  $\hbar^2 k^2 / 2m$ , so the energy of the shell is

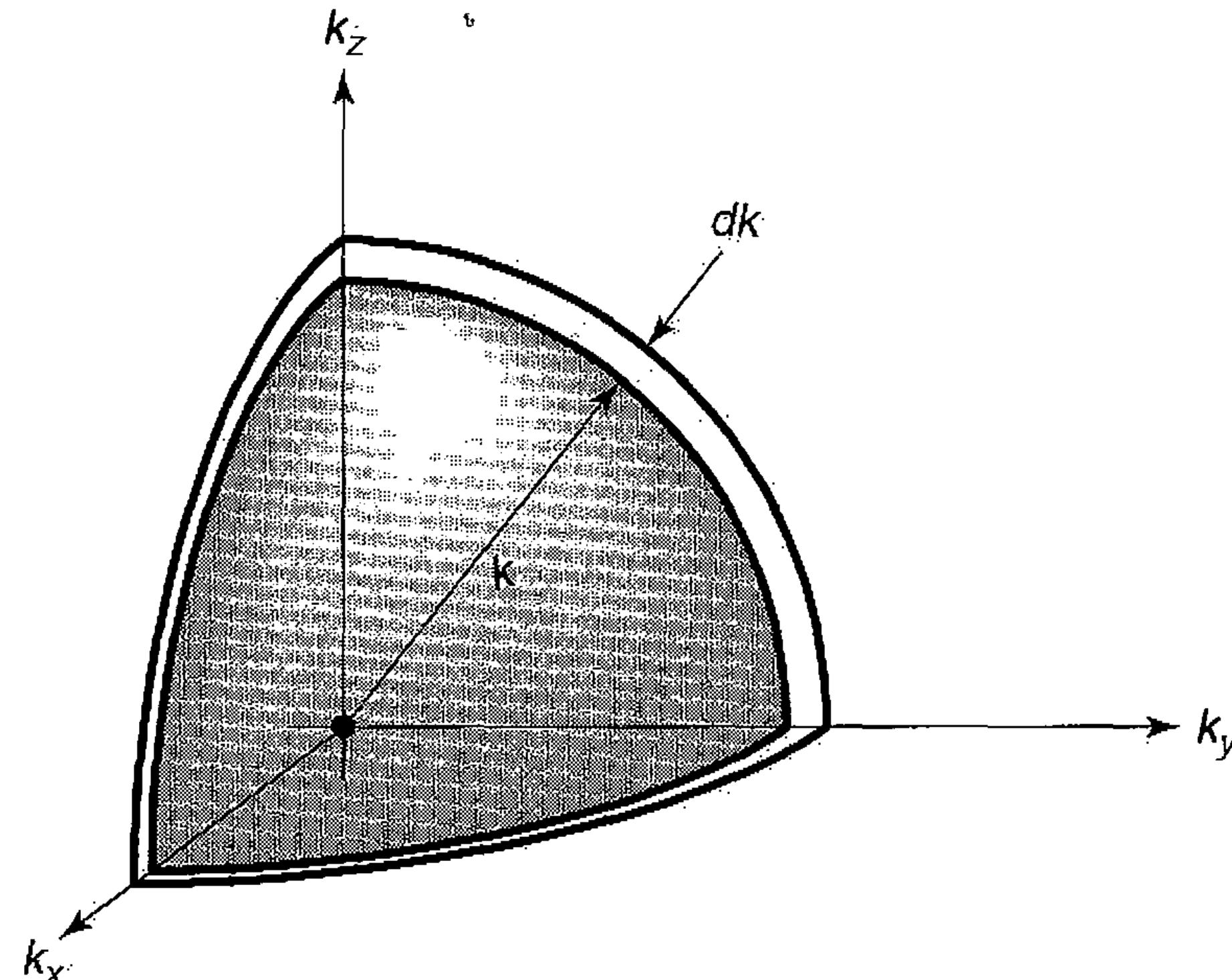
$$dE = \frac{\hbar^2 k^2}{2m} \frac{V}{\pi^2} k^2 dk,$$

and hence the total energy is

$$E_{\text{tot}} = \frac{\hbar^2 V}{2\pi^2 m} \int_0^{k_F} k^4 dk = \frac{\hbar^2 k_F^5 V}{10\pi^2 m} = \frac{\hbar^2 (3\pi^2 N q)^{5/3}}{10\pi^2 m} V^{-2/3}.$$

This quantum mechanical energy plays a role rather analogous to the internal *thermal* energy ( $U$ ) of an ordinary gas. In particular, it exerts a *pressure* on the walls, for if the box expands by an amount  $dV$ , the total energy decreases:

$$dE_{\text{tot}} = -\frac{2}{3} \frac{\hbar^2 (3\pi^2 N q)^{5/3}}{10\pi^2 m} V^{-5/3} dV = -\frac{2}{3} E_{\text{tot}} \frac{dV}{V},$$



and this shows up as work done on the outside ( $dW = P dV$ ) by the quantum pressure  $P$ . Evidently

$$P = \frac{2}{3} \frac{E_{\text{tot}}}{V} = \frac{2}{3} \frac{\hbar^2 k_F^5}{10\pi^2 m} = \frac{(3\pi^2)^{2/3} \hbar^2}{5m} \rho^{5/3}.$$

## Degeneracy Pressure

Another reading task 😞: Bloch's theory

# Quantum Statistical Mechanics

The fundamental assumption of statistical mechanics is that in thermal equilibrium every distinct state with the same *total* energy,  $E$ , is equally probable. Random thermal motions constantly shift energy from one particle to another, and from one form (rotational, kinetic, vibrational, etc.) to another, but (absent external influences) the *total* is fixed by conservation of energy. The assumption (and it's a *deep* one, worth thinking about) is that this continual redistribution of energy does not favor any particular state. The temperature,  $T$ , is simply a measure of the total energy of a system in thermal equilibrium. The only new twist introduced by quantum mechanics has to do with *how we count the distinct states* (it's actually *easier* than in the classical theory, because the states are generally discrete), and this depends critically on whether the particles involved are distinguishable, identical bosons, or identical fermions.

# An Example

Suppose we have just *three* noninteracting particles (all of mass  $m$ ) in the one-dimensional infinite square well. The total energy is

$$E = E_A + E_B + E_C = \frac{\pi^2 \hbar^2}{2m a^2} (n_A^2 + n_B^2 + n_C^2)$$

where  $n_A$ ,  $n_B$ , and  $n_C$  are positive integers. Now suppose,  $E = 363(\pi^2\hbar^2/2ma^2)$ ,

$$n_A^2 + n_B^2 + n_C^2 = 363.$$

There are, as it happens, 13 combinations of three positive integers, the sum of whose squares is 363: All three could be 11, two could be 13 and one 5

(which occurs in three permutations), one could be 19 and two 1 (again, three permutations), or one could be 17, one 7, and one 5 (six permutations). Thus  $(n_A, n_B, n_C)$  is one of the following:

(11, 11, 11).

Config. 1

$$(13, 13, 5), (13, 5, 13), (5, 13, 13)$$

## Config. 2

$$(1, 1, 19), (1, 19, 1), (19, 1, 1)$$

## Config. 3

$(5, 7, 17), (5, 17, 7), (7, 5, 17), (7, 17, 5), (17, 5, 7), (17, 7, 5)$ , Config. 4

## Config. 4

If the particles are *distinguishable*, each of these represents a distinct quantum state, and the fundamental assumption of statistical mechanics says that in thermal equilibrium they are all equally likely. But I'm not interested in knowing *which* particle is in *which* (one-particle) state, only the total *number* of particles in each state—the **occupation number**,  $N_n$ , for the state  $\psi_n$ . The collection of all occupation numbers for a given 3-particle state we will call the configuration. If all three are in  $\psi_{11}$ , the configuration is

$$(0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 3, 0, 0, 0, 0, 0, 0, 0, \dots)$$

(i.e.,  $N_{11} = 3$ , all others zero). If two are in  $\psi_{13}$  and one is in  $\psi_5$ , the configuration is

$$(0, 0, 0, 0, 1, 0, 0, 0, 0, 0, 0, 2, 0, 0, 0, \dots)$$

(i.e.,  $N_5 = 1$ ,  $N_{13} = 2$ , all others zero).

# Quantum Statistical Mechanics

## An Example ...

If two are in  $\psi_1$  and one is in  $\psi_{19}$ , the configuration is

$$(2, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 1, 0, \dots), \quad [5.71]$$

(i.e.,  $N_1 = 2$ ,  $N_{19} = 1$ , all others zero). And if there is one particle in  $\psi_5$ , one in  $\psi_7$ , and one in  $\psi_{17}$ , the configuration is

$$(0, 0, 0, 0, 1, 0, 1, 0, 0, 0, 0, 0, 0, 0, 0, 0, 1, 0, 0, \dots). \quad [5.72]$$

(i.e.,  $N_5 = N_7 = N_{17} = 1$ , all others zero.) Of these, the last is the *most probable* configuration, because it can be achieved in six different ways, whereas the middle two occur three ways, and the first only one. if we select one of these three particles at random, what is the probability ( $P_n$ ) of getting a specific (allowed) energy  $E_n$ ? The only way you can get  $E_1$  is if it's in the third configuration the

chances of the system being in that configuration are 3 in 13, and in that configuration the probability of getting  $E_1$  is  $2/3$ , so  $P_1 = (3/13) \times (2/3) = 2/13$ . You could get  $E_5$  either from configuration 2—chances 3 in 13—with probability  $1/3$ , or from configuration 4—chances 6 in 13—with probability  $1/3$ , so  $P_5 = (3/13) \times (1/3) + (6/13) \times (1/3) = 3/13$ . You can only get  $E_7$  from configuration 4:  $P_7 = (6/13) \times (1/3) = 2/13$ . Likewise,  $E_{11}$  comes only from the first configuration—chances 1 in 13—with probability 1:  $P_{11} = (1/13)$ . Similarly,  $P_{13} = (3/13) \times (2/3) = 2/13$ ,  $P_{17} = (6/13) \times (1/3) = 2/13$ , and  $P_{19} = (3/13) \times (1/3) = 1/13$ . As a check, note that

$$P_1 + P_5 + P_7 + P_{11} + P_{13} + P_{17} + P_{19} = \frac{2}{13} + \frac{3}{13} + \frac{2}{13} + \frac{1}{13} + \frac{2}{13} + \frac{2}{13} + \frac{1}{13} = 1.$$

That's when the particles are distinguishable. If in fact they are *identical fermions*, the antisymmetrization requirement (leaving aside spin, for simplicity—or assuming they are all in the *same* spin state, if you prefer) excludes the first three configurations (which assign two—or, worse still, three—particles to the same state), and there is just *one* state in the fourth configuration

For identical fermions, then,  $P_5 = P_7 = P_{17} = 1/3$  (and again the sum of the probabilities is 1). On the other hand, if they are *identical bosons* the symmetrization requirement allows for *one* state in each configuration so  $P_1 = (1/4) \times (2/3) = 1/6$ ,  $P_5 = (1/4) \times (1/3) + (1/4) \times (1/3) = 1/6$ ,  $P_7 = (1/4) \times (1/3) = 1/12$ ,  $P_{11} = (1/4) \times (1) = 1/4$ ,  $P_{13} = (1/4) \times (2/3) = 1/6$ ,  $P_{17} = (1/4) \times (1/3) = 1/12$ , and  $P_{19} = (1/4) \times (1/3) = 1/12$ . As always, the sum is 1.

The purpose of this example was to show you how the counting of states depends on the nature of the particles. In one respect it was actually *more complicated* than the realistic situation, in which  $N$  is a huge number. For as  $N$  grows, the most probable configuration (in this example,  $N_5 = N_7 = N_{17} = 1$ , for the case of distinguishable particles) becomes *overwhelmingly* more likely than its competitors, so that, for statistical purposes, we can afford to ignore the others altogether: The distribution of individual particle energies, at equilibrium, is simply their distribution in the most probable configuration. (If this were true for  $N = 3$ —which, obviously, it is *not*—we would conclude that  $P_5 = P_7 = P_{17} = 1/3$  for the case of distinguishable particles.)

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## The General Case

Now consider an arbitrary potential, for which the one-particle energies are  $E_1, E_2, E_3, \dots$ , with degeneracies  $d_1, d_2, d_3, \dots$  (i.e., there are  $d_n$  distinct one-particle states with energy  $E_n$ ). Suppose we put  $N$  particles (all with the same mass) into this potential; we are interested in the configuration  $(N_1, N_2, N_3, \dots)$ , for which there are  $N_1$  particles with energy  $E_1$ ,  $N_2$  particles with energy  $E_2$ , and so on.

**Question:** How many different ways can this be achieved (or, more precisely, how many distinct states correspond to this particular configuration)? The answer,  $Q(N_1, N_2, N_3, \dots)$ , depends on whether the particles are distinguishable, identical fermions, or identical bosons, so we'll treat the three cases separately.

First, assume the particles are *distinguishable*. How many ways are there to select (from the  $N$  available candidates) the  $N_1$  to be placed in the first “bin”?

**Answer:** the **binomial coefficient**, “ $N$  choose  $N_1$ ,”

$$\binom{N}{N_1} = \frac{N!}{N_1!(N - N_1)!}.$$

For there are  $N$  ways to pick the first particle, leaving  $(N - 1)$  for the second, and so on:

$$N(N - 1)(N - 2)\dots(N - N_1 + 1) = \frac{N!}{(N - N_1)!}.$$

However, this counts separately the  $N_1!$  different *permutations* of the  $N_1$  particles, whereas we don't care whether number 37 was picked on the first draw, or on the 29th draw; so we divide by  $N_1!$  Now, how many different ways can those  $N_1$  particles be arranged *within* the first bin? Well, there

are  $d_1$  states in the bin, so each particle has  $d_1$  choices; evidently there are  $(d_1)^{N_1}$  possibilities in all. Thus the number of ways to put  $N_1$  particles, selected from a total population of  $N$ , into a bin containing  $d_1$  distinct options, is

$$\frac{N!d_1^{N_1}}{N_1!(N - N_1)!}.$$

The same goes for bin 2, of course, except that there are now only  $(N - N_1)$  particles left to work with:

$$\frac{(N - N_1)!d_2^{N_2}}{N_2!(N - N_1 - N_2)!},$$

and so on. It follows that

$$\begin{aligned} Q(N_1, N_2, N_3, \dots) &= \frac{N!d_1^{N_1}}{N_1!(N - N_1)!} \frac{(N - N_1)!d_2^{N_2}}{N_2!(N - N_1 - N_2)!} \frac{(N - N_1 - N_2)!d_3^{N_3}}{N_3!(N - N_1 - N_2 - N_3)!} \dots \\ &= N! \frac{d_1^{N_1} d_2^{N_2} d_3^{N_3} \dots}{N_1! N_2! N_3! \dots} = N! \prod_{n=1}^{\infty} \frac{d_n^{N_n}}{N_n!}. \end{aligned}$$

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## Identical Fermions & Bosons

The problem is a lot easier for *identical fermions*. Because they are indistinguishable, it doesn't matter *which* particles are in *which* states—the antisymmetrization requirement means that there is just *one*  $N$ -particle state in which a specific set of one-particle states are occupied. Moreover, only one particle can occupy any given state. There are

$$\binom{d_n}{N_n}$$

ways to choose the  $N_n$  occupied states in the  $n$ th bin,

$$Q(N_1, N_2, N_3, \dots) = \prod_{n=1}^{\infty} \frac{d_n!}{N_n!(d_n - N_n)!}.$$

The calculation is hardest for the case of *identical bosons*. Again, the symmetrization requirement means that there is just one  $N$ -particle state in which a specific set of one-particle states are occupied, but this time there is no restriction on the number of particles that can share the same one-particle state. For the  $n$ th bin, the question becomes: How many different ways can we assign  $N_n$  identical particles to  $d_n$  different slots? There are many tricks to solve this combinatorial problem; an especially clever method is as follows: Let dots represent particles and crosses represent partitions, so that, for example, if  $d_n = 5$  and  $N_n = 7$ ,

• • × • × • • • × • ×

would indicate that there are two particles in the first state, one in the second, three

in the third, one in the fourth, and none in the fifth. Note that there are  $N_n$  dots, and  $(d_n - 1)$  crosses (partitioning the dots into  $d_n$  groups). If the individual dots and crosses were *labeled*, there would be  $(N_n + d_n - 1)!$  different ways to arrange them. But for our purposes the dots are all equivalent—permuting them ( $N_n!$  ways) does not change the state. Likewise, the crosses are all equivalent—permuting them  $((d_n - 1)!$  ways) changes nothing. So there are in fact

$$\frac{(N_n + d_n - 1)!}{N_n!(d_n - 1)!} = \binom{N_n + d_n - 1}{N_n}$$

distinct ways of assigning the  $N_n$  particles to the  $d_n$  one-particle states in the  $n$ th bin, and we conclude that

$$Q(N_1, N_2, N_3, \dots) = \prod_{n=1}^{\infty} \frac{(N_n + d_n - 1)!}{N_n!(d_n - 1)!}$$

# Quantum Statistical Mechanics

## The Most Probable Configuration

In thermal equilibrium, every state with a given total energy  $E$  and a given particle number  $N$  is equally likely. So the *most probable configuration*  $(N_1, N_2, N_3, \dots)$  is the one that can be achieved in the largest number of different ways—it is that particular configuration for which  $Q(N_1, N_2, N_3, \dots)$  is a maximum, subject to the constraints

$$\sum_{n=1}^{\infty} N_n = N,$$

$$\sum_{n=1}^{\infty} N_n E_n = E.$$

and

The problem of maximizing a function  $F(x_1, x_2, x_3, \dots)$  of several variables, subject to the constraints  $f_1(x_1, x_2, x_3, \dots) = 0, f_2(x_1, x_2, x_3, \dots) = 0$ , etc., is most conveniently handled by the method of **Lagrange multipliers**. We introduce the new function

$$G(x_1, x_2, x_3, \dots, \lambda_1, \lambda_2, \dots) \equiv F + \lambda_1 f_1 + \lambda_2 f_2 + \dots,$$

and set *all* its derivatives equal to zero:

$$\frac{\partial G}{\partial x_n} = 0; \quad \frac{\partial G}{\partial \lambda_n} = 0.$$

In our case it's a little easier to work with the *logarithm* of  $Q$ , instead of  $Q$  itself—this turns the *products* into *sums*. Since the logarithm is a monotonic function of its argument, the maxima of  $Q$  and  $\ln(Q)$  occur at the same point. So we let

$$G \equiv \ln(Q) + \alpha \left[ N - \sum_{n=1}^{\infty} N_n \right] + \beta \left[ E - \sum_{n=1}^{\infty} N_n E_n \right],$$

where  $\alpha$  and  $\beta$  are the Lagrange multipliers. Setting the derivatives with respect to  $\alpha$  and  $\beta$  equal to zero merely reproduces the constraints; it remains, then, to set the derivative with respect to  $N_n$  equal to zero.

If the particles are *distinguishable*, then

$$G = \ln(N!) + \sum_{n=1}^{\infty} [N_n \ln(d_n) - \ln(N_n!)]$$

$$+ \alpha \left[ N - \sum_{n=1}^{\infty} N_n \right] + \beta \left[ E - \sum_{n=1}^{\infty} N_n E_n \right].$$

Assuming the relevant occupation numbers ( $N_n$ ) are large, we can invoke **Stirling's approximation**:

$$\ln(z!) \approx z \ln(z) - z \quad \text{for } z \gg 1,$$

to write  $G \approx \sum_{n=1}^{\infty} [N_n \ln(d_n) - N_n \ln(N_n) + N_n - \alpha N_n - \beta E_n N_n]$   
 $+ \ln(N!) + \alpha N + \beta E.$

It follows that

$$\frac{\partial G}{\partial N_n} = \ln(d_n) - \ln(N_n) - \alpha - \beta E_n.$$

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Setting this equal to zero, and solving for  $N_n$ , we conclude that the *most probable occupation numbers*, for distinguishable particles, are

$$N_n = d_n e^{-(\alpha + \beta E_n)}.$$

If the particles are *identical fermions*,

$$G = \sum_{n=1}^{\infty} \{ \ln(d_n!) - \ln(N_n!) - \ln[(d_n - N_n)!] \} + \alpha \left[ N - \sum_{n=1}^{\infty} N_n \right] + \beta \left[ E - \sum_{n=1}^{\infty} N_n E_n \right]$$

This time we must assume not only that  $N_n$  is large, but also that  $d_n \gg N_n$ , so that Stirling's approximation applies to both terms. In that case

$$\begin{aligned} G \approx & \sum_{n=1}^{\infty} \left[ \ln(d_n!) - N_n \ln(N_n) + N_n - (d_n - N_n) \ln(d_n - N_n) \right. \\ & \left. + (d_n - N_n) - \alpha N_n - \beta E_n N_n \right] + \alpha N + \beta E, \end{aligned}$$

so

$$\frac{\partial G}{\partial N_n} = -\ln(N_n) + \ln(d_n - N_n) - \alpha - \beta E_n.$$

Setting this equal to zero, and solving for  $N_n$ , we find the *most probable occupation numbers* for identical fermions:

$$N_n = \frac{d_n}{e^{(\alpha + \beta E_n)} + 1}.$$

Finally, if the particles are *identical bosons*, then we have

$$\begin{aligned} G = & \sum_{n=1}^{\infty} \{ \ln[(N_n + d_n - 1)!] - \ln(N_n!) - \ln[(d_n - 1)!] \} \\ & + \alpha \left[ N - \sum_{n=1}^{\infty} N_n \right] + \beta \left[ E - \sum_{n=1}^{\infty} N_n E_n \right]. \end{aligned}$$

Assuming (as always) that  $N_n \gg 1$ , and using Stirling's approximation:

$$\begin{aligned} G \approx & \sum_{n=1}^{\infty} \{ (N_n + d_n - 1) \ln(N_n + d_n - 1) - (N_n + d_n - 1) - N_n \ln(N_n) \\ & + N_n - \ln[(d_n - 1)!] - \alpha N_n - \beta E_n N_n \} + \alpha N + \beta E, \end{aligned}$$

so

$$\frac{\partial G}{\partial N_n} = \ln(N_n + d_n - 1) - \ln(N_n) - \alpha - \beta E_n.$$

Setting this equal to zero, and solving for  $N_n$ , we find the *most probable occupation numbers* for identical bosons:

$$N_n = \frac{d_n - 1}{e^{(\alpha + \beta E_n)} - 1}.$$

# Quantum Statistical Mechanics

## Physical Significance of $\alpha$ and $\beta$

The parameters  $\alpha$  and  $\beta$  came into the story as Lagrange multipliers, associated with the total number of particles and the total energy, respectively. To carry out the summation, however, we need to know the allowed energies ( $E_n$ ), and their degeneracies ( $d_n$ ), for the potential in question. As an example, I'll work out the case of an **ideal gas**—a large number of noninteracting particles, all with the same mass, in the three dimensional infinite square well. This will motivate the physical interpretation of  $\alpha$  and  $\beta$ .

we found the allowed energies

$$E_k = \frac{\hbar^2}{2m} k^2,$$

where

$$\mathbf{k} = \left( \frac{\pi n_x}{l_x}, \frac{\pi n_y}{l_y}, \frac{\pi n_z}{l_z} \right).$$

As before, we convert the sum into an integral, treating  $\mathbf{k}$  as a continuous variable, with one state (or, for spin  $s$ ,  $2s + 1$  states) per volume  $\pi^3/V$  of  $k$ -space. Taking as our “bins” the spherical shells in the first octant the “degeneracy” the “degeneracy” (that is, the number of states in the bin) is

$$d_k = \frac{1}{8} \frac{4\pi k^2 dk}{(\pi^3/V)} = \frac{V}{2\pi^2} k^2 dk.$$

For distinguishable particles

$$N = \frac{V}{2\pi^2} e^{-\alpha} \int_0^\infty e^{-\beta \hbar^2 k^2 / 2m} k^2 dk = V e^{-\alpha} \left( \frac{m}{2\pi\beta\hbar^2} \right)^{3/2}.$$

so

$$e^{-\alpha} = \frac{N}{V} \left( \frac{2\pi\beta\hbar^2}{m} \right)^{3/2}.$$

The second constraint

$$E = \frac{V}{2\pi^2} e^{-\alpha} \frac{\hbar^2}{2m} \int_0^\infty e^{-\beta \hbar^2 k^2 / 2m} k^4 dk = \frac{3V}{2\beta} e^{-\alpha} \left( \frac{m}{2\pi\beta\hbar^2} \right)^{3/2}.$$

or,

$$E = \frac{3N}{2\beta}.$$

This result is reminiscent of the classical formula for the average kinetic energy of an atom at temperature  $T$ :

$$\frac{E}{N} = \frac{3}{2} k_B T,$$

where  $k_B$  is the Boltzmann constant. This suggests that  $\beta$  is related to the *temperature*:

$$\beta = \frac{1}{k_B T}.$$

# Quantum Statistical Mechanics

## Physical Significance of $\alpha$ and $\beta$

It is customary to replace  $\alpha$  by the so-called **chemical potential**,

$$\mu(T) \equiv -\alpha k_B T,$$

the *most probable number of particles in a particular (one-particle) state with energy  $\epsilon$*

	<b>MAXWELL-BOLTZMANN</b>
$n(\epsilon) = \begin{cases} e^{-(\epsilon-\mu)/k_B T} & \\ \frac{1}{e^{(\epsilon-\mu)/k_B T} + 1} & \end{cases}$	<b>FERMI-DIRAC</b>
	<b>BOSE-EINSTEIN</b>

The **Maxwell-Boltzmann distribution** is the classical result, for *distinguishable* particles; the **Fermi-Dirac distribution** applies to *identical fermions*, and the **Bose-Einstein distribution** is for *identical bosons*.

The Fermi-Dirac distribution has a particularly simple behavior as  $T \rightarrow 0$ :

$$e^{(\epsilon-\mu)/k_B T} \rightarrow \begin{cases} 0, & \text{if } \epsilon < \mu(0), \\ \infty, & \text{if } \epsilon > \mu(0). \end{cases}$$

so

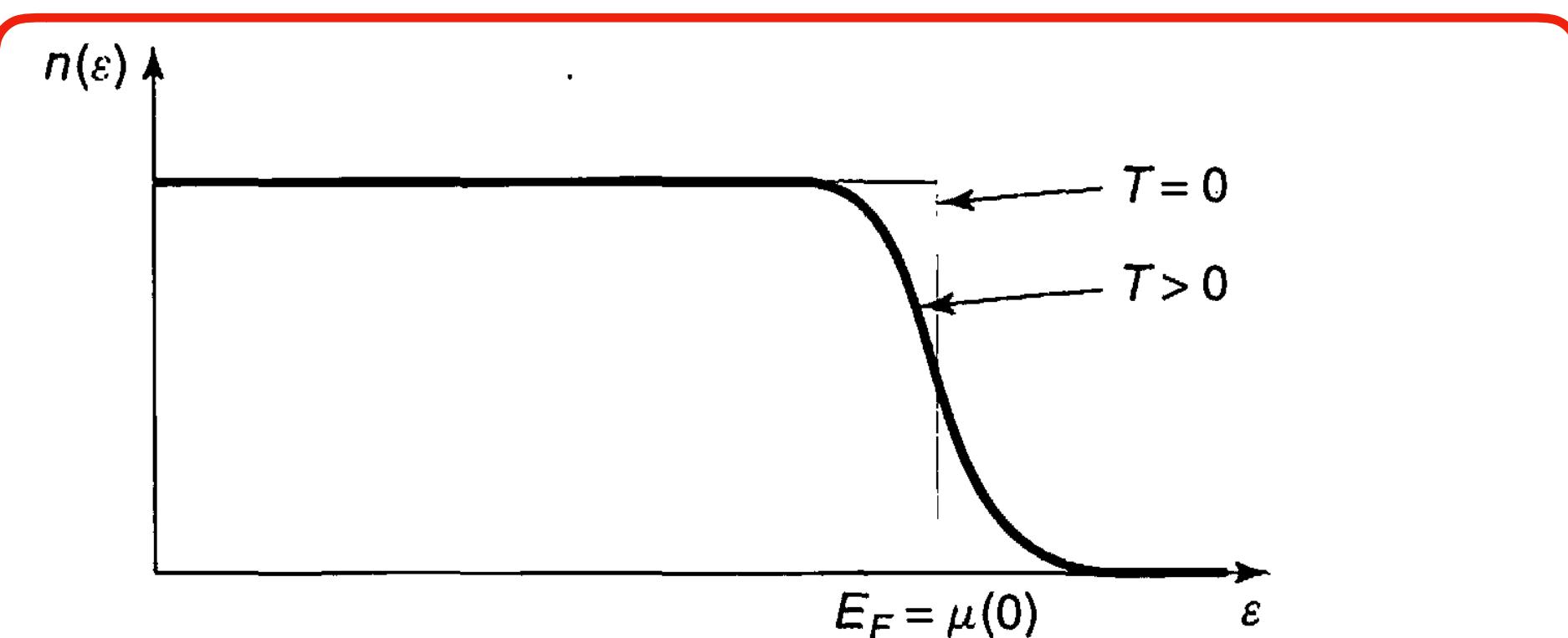
$$n(\epsilon) \rightarrow \begin{cases} 1, & \text{if } \epsilon < \mu(0), \\ 0, & \text{if } \epsilon > \mu(0). \end{cases}$$

All states are filled, up to an energy  $\mu(0)$ , and none are occupied for energies above this

Evidently the chemical potential at absolute zero is precisely the Fermi energy:

$$\mu(0) = E_F.$$

As the temperature rises, the Fermi-Dirac distribution “softens” the cutoff, as indicated by the rounded curve



Fermi-Dirac distribution for  $T = 0$  and for  $T$  somewhat above zero.

Returning now to the special case of an ideal gas, for distinguishable particles we found that the total energy at temperature  $T$  is

$$E = \frac{3}{2} N k_B T.$$

and the chemical potential is  $\mu(T) = k_B T \left[ \ln \left( \frac{N}{V} \right) + \frac{3}{2} \ln \left( \frac{2\pi\hbar^2}{mk_B T} \right) \right]$ .

Yet another reading task 😞😞: The Blackbody Spectrum