

**NOTES 2: MICROSCOPIC MECHANICS AND THE COUPLING TO THERMODYNAMICS:
STATISTICAL MECHANICS AND THE SOLID-STATE HIERARCHY**

- Macroscopic definition

- spatial extent of solid-state system

- external "forces" being applied

- important thermodynamic quantities in response to forces:

- 1) Quasi-equilibrium formulation if response of entire system is weak.

- 2) Non-equilibrium formulation (transport) if response of portion of system is strong.

- heat is almost always important since there are usually many ways microscopically to absorb and store energy, and to couple it to potential or kinetic energy.

- Microscopic definition

- Identify particles that determine thermodynamic variables and response to external forces.

- Scale down forces from macroscopic to microscopic level

- Identify interaction between these particles and external forces, and between themselves.

- Determine distinguishability of particles in terms of interparticle separation d and de Broglie wavelength λ_d

$$d \gg \lambda_d \rightarrow \lambda_d \text{ distinguishable, } \lambda_d = \frac{h}{p}; \text{ where } h \text{ is Planck's constant } [6.626 \times 10^{-34} \text{ J-s}]$$

and p is the particle classical momentum.

$$d \ll \lambda_d \rightarrow \lambda_d \text{ indistinguishable, } \frac{p^2}{2m} = u_k \quad u_k = \text{kinetic energy}$$

- Formulate mechanical (dynamical) description

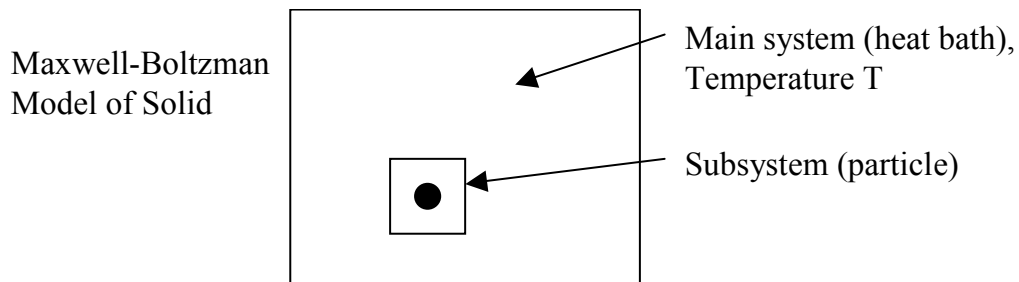
- (1) distinguishable particles \rightarrow classical mechanics (Newton's Law): $\mathbf{F} = d\mathbf{p}/dt = m d^2\mathbf{r}/dt^2$ where \mathbf{F} is the force, \mathbf{p} is the momentum and \mathbf{r} is the position

- (2) indistinguishable particles \rightarrow quantum mechanics (Schrödinger equation):

$$\frac{-\hbar^2}{2m} \nabla^2 \psi + V\psi = U\psi \text{ where } \psi \text{ is the particle spatial probability amplitude (i.e., the}$$

“wavefunction”), V is particle potential energy, and U is the total energy. Solutions for ψ are called “eigenfunctions” or, sometimes, *modes* because of their wave nature.

- Relate microscopic to macroscopic (statistical mechanics).
- Motivation: the number of particles in any solid system is far too large to solve mechanics exactly. So focus on a judiciously chosen microscopic subsystem in which the mechanics (be it classical or quantum mechanical) is tractable (see sketch below). The remainder of the system is called the “bath” and because of its large number of particles and modes it can be assigned a macroscopic temperature T_b . Note: in the simplest case the subsystem is a single particle; but as we shall soon see, the subsystem can be also be a single-particle mechanical mode shared in common by many *indistinguishable* particles (the case of electrons in a metal). It can also be a multi-particle mode in which the excitation of the mode is distributed indistinguishably over the many particles (quantized lattice waves, or phonons).



Boltzmann Density Function (Exponential pdf)

- Independent of the subsystem, we can apply statistical reasoning to the behavior of the subsystem based on the fact that the “bath” provides an uncountably large number of internal modes or ways to exchange energy with the subsystem. Based on this reasoning, Boltzmann showed that the occupation of the subsystem could be described by the following *probability density function (pdf)*,

$$P(U) = C \exp(-U/k_B T)$$

where U is the total energy (potential+ kinetic) of the subsystem. C is a normalization constant determined by the condition

$$\int_0^{\infty} P(U) dU = 1 = \int_0^{\infty} C \exp(-U / k_B T) dU$$

Evaluation of the latter integral yields $C = (k_B T)^{-1}$.

The Boltzmann pdf is identical to the exponential pdf of probability theory and, as such, has the following special properties (to be reviewed in the HW):

(1) The mean value of U , also called the expectation value in probability theory $E\{U\}$ is

$$\text{found to be } \langle U \rangle = E\{U\} = (k_B T)^{-1} \int_0^{\infty} U \exp(-U/k_B T) dU = k_B T$$

(2) The rms deviation of U from the mean value is found to be

$$\Delta U = [\langle (U - \langle U \rangle)^2 \rangle]^{1/2} = \left((k_B T)^{-1} \int_0^{\infty} [U - \langle U \rangle]^2 \exp(-U/k_B T) dU \right)^{1/2} = k_B T.$$

So we have the remarkable result that the root mean-square deviation equals the mean !

In practice U is always expressed in terms of the mechanical variables, be they classical or quantum mechanical.

Intuitive Justification for Boltzmann pdf:

Subsystem is in equilibrium with bath \rightarrow low energy states favored because bath will rapidly absorb high energy excess. In other words, there are more ways for high-energy states to “thermalize”, so they should have much lower probability of occupation.

The first test of the Boltzmann statistics was applied to systems (e.g., gases) in which the subsystem is best chosen as an individual particle, and the low concentration and weak interparticle forces allow the application of classical (Newtonian) mechanics. The total energy is all kinetic $U = (1/2) m v^2 = p^2/2m$ where $v = |\mathbf{v}|$ is the magnitude of the vector velocity and $p = |\mathbf{p}|$ is the magnitude of the vector momentum. The pdf is now given by

$$P(\mathbf{v}) d\mathbf{v} = C \exp(-m|\mathbf{v}|^2/2k_B T) d\mathbf{v}$$

Which is a scalar function of a vector stochastic variable, the velocity. The normalization factor is now given by

$$\int_0^{\infty} \int_0^{\pi} \int_0^{2\pi} C \exp(-m v^2 / 2k_B T) v^2 \sin \theta dv d\theta d\phi = 1$$

Evaluation of this integral results in $C (2\pi k_B T/m)^{3/2} = 1$. So the resulting pdf has the form

$$P(\mathbf{v}) d\mathbf{v} = (m/2\pi k_B T)^{3/2} \exp(-m v^2 / 2k_B T) d\mathbf{v}$$

This is, in fact, a 3-dim form of the famous Gaussian pdf of probability theory.

For solids it is rare that any mechanical quantity be treated as a continuous stochastic variable. A more common situation is that U is a function of a *discrete* variable, sometimes

classical, sometimes quantum mechanical. For an independent particle that is not mechanically coupled or quantum-mechanically correlated to any others in the system, we can again consider the particle itself as a subsystem (albeit, a very small one) coupled to the rest of the system (heat bath) through heat transfer.

The Boltzman probability of occupancy of the subsystem energy level U_r is then

$$P_r = C \exp(-U_r/k_B T)$$

where $U_r \rightarrow$ total energy of subsystem in that state [i.e., $U_r = U_k + U_p$ (kinetic & potential energy), and C is the normalization constant; defined by

$$\sum_r P_r = C \sum_r \exp(-U_r/k_B T) = 1 \text{ . or } C = \frac{1}{\sum_r \exp(-U_r/k_B T)}$$

Thermodynamic averages (e.g. extensive quantities, Y_i) are taken as a mean value. For example,

the mean energy of the subsystem is $\langle U \rangle = \frac{\sum_r U_r \exp(-U_r/k_B T)}{\sum_r \exp(-U_r/k_B T)}$. Other extensive quantities

must be expressed in terms of the energy, or else both the U_r and Y_r are expressed in terms of microscopic mechanical or electromagnetic quantities.

$$\langle Y_r \rangle = \sum_r Y_r P_r = \frac{\sum_r Y_r \exp(-U_r/k_B T)}{\sum_r \exp(-U_r/k_B T)}$$

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Example: Discrete Boltzman density with a known energy distribution

Suppose we have a particle in which the energy levels are distributed in a “ladder” such that $u_n = n u_0$, where n is an integer and u_0 is a minimum (“ground state”) energy. The Boltzman pdf is

given by $P(u_n) = C \exp(-nu_0/k_B T)$ where $C^{-1} = \sum_{n=0}^{\infty} \exp(\frac{-nu_0}{k_B T})$

From elementary calculus this is an infinite “geometric” series of terms r^n where $|r| < 1$, so that the series sums to $\sum_{n=0}^{\infty} \exp(\frac{-nu_0}{k_B T}) = \frac{1}{1-r} = \frac{1}{1-\exp(-u_0/k_B T)}$. So the Boltzman pdf is

$$P(u_n) = [1 - \exp(\frac{-u_0}{k_B T})] \exp(-nu_0/k_B T).$$

The mean energy is then simply $\langle u \rangle = [1 - \exp(\frac{-u_0}{k_B T})] \sum_{n=0}^{\infty} n u_0 \exp(-nu_0/k_B T)$

While at first appearing formidable, this sum evaluates beautifully with a trick:

Note: $nu_0 \exp(-nu_0/k_B T) = k_B T^2 d/dT \{ \exp(-nu_0/k_B T) \}$. So by exchanging the order of summation and differentiation (valid for well-behaved functions), we get

$$\begin{aligned} \langle u \rangle &= [1 - \exp(-u_0/k_B T)] (-k_B T^2) \frac{d}{dT} \sum_{n=0}^{\infty} \exp(-nu_0/k_B T) = \\ &= [1 - \exp(-u_0/k_B T)] (k_B T^2) \frac{d}{dT} \cdot \frac{1}{1 - \exp(-u_0/k_B T)} = [1 - \exp(-u_0/k_B T)] \cdot \frac{u_0 \exp(-u_0/k_B T)}{[1 - \exp(-u_0/k_B T)]^2} \end{aligned}$$

$$\text{But this simplifies to } \langle u \rangle = \frac{u_0 \exp(-u_0/k_B T)}{[1 - \exp(-u_0/k_B T)]} = \frac{u_0}{\exp(u_0/k_B T) - 1}$$

The factor $[\exp(u_0/k_B T) - 1]^{-1}$ is called the Planck function. We will see this again when dealing with quantized lattice waves, or phonons. Note that in the “classical” limit where $u_0 \ll k_B T$, we can expand the denominator $\exp(u_0/k_B T) - 1 \approx 1 + u_0/k_B T - 1 = u_0/k_B T$

And we get $\langle u \rangle \rightarrow k_B T$ - the same result as for the Boltzman continuous pdf (as expected) !

The Effect of Quantum Identity (Quantum Statistics)

- It is rather clear when the nanomechanics of a particle or other subsystem must be evaluated by quantum mechanics based on spatial distinguishability. More subtle is the fact that the statistical analysis depends on the quantum *identity* (i.e., as expressed by the spin) of the particles at hand.
 - (1) Spin-free (classical) particles → classical (Boltzman) pdf
 - (2) Particles with spin → Boltzman pdf but with important constraints
 - a) half-odd integral spin (1/2, 3/2 ...) → Fermi-Dirac distribution
 - b) integral spin (1,2....) → Bose-Einstein distribution
- The quantum identity is stated for Fermions by the Pauli exclusion principle: no two Fermions can occupy the same (quantum mechanical) space-spin state.
- Important point: independent of quantum identity, Boltzmann statistical argument about the subsystem interacting with a “bath” is still valid. The energy of each particle (or mode occupied by many particles) is still a good statistical descriptor. It is how the pdf is summed that changes. For particles with spin, *the number of them in each state is also important*

Indistinguishable-Particle Constraints

- We apply the Boltzman reasoning not to a single particle because that is indistinguishable. Instead, we apply it to the *entire population* of such particles,

$$P_r = \frac{e^{-U_r/k_B T}}{\sum_r e^{-U_r/k_B T}} = \frac{\exp\left(-\sum_i^N u_i/k_B T\right)}{\sum_r \exp\left(-\sum_i^N u_i/k_B T\right)}$$

where u_i is the energy of the i th particle of a given spin and N is the total number of particles in the subsystem. Next we note that the use of quantum mechanics and single-particle states allows us to index the particle states by the wavevector (or quantum number j)

$$\text{so that } \sum_i^N u_i \rightarrow \sum_j n_j u_j$$

We also note that such indexing allows (requires) that the overall state of the system be completely specified by enumerating the number of particles n_j in each quantum state

$$\text{so that } \sum_r \rightarrow \sum_{n_j}^N \text{ where } \sum^N \text{ means a "restricted" sum, subject to } \sum_j n_j = N$$

$$P_r \rightarrow P_{n_j} = \frac{\exp\left(-\sum_j n_j u_j / k_B T\right)}{\sum_{n_j}^N \exp\left(-\sum_j n_j u_j / k_B T\right)}$$

1) for 1/2-odd-integral spin (Fermions): $n_j = 0$ or 1

2) for even-integral spin (Bosons): $n_j = \text{any value up to } N$

The resulting P_{n_j} is more complex than that for Boltzman statistics and once summed over becomes a distribution function (recall from probability theory that distribution functions result from partial summation or integration over pdfs).

Remarkably, certain mean values become quite simple: for example, the number of particles occupying quantum states having energy u_k is defined by the symbol $\langle n_{u_k} \rangle \equiv \langle N_k \rangle$, and we can write

$$\langle N_k \rangle = \frac{\sum_{n_j}^N n_k g_k \exp\left(-\sum_{j=k} n_j u_j / k_B T\right)}{\sum_{n_j}^N \exp\left(-\sum_{j=k} n_j u_j / k_B T\right)}$$

where g is the quantum degeneracy factor, or the number of distinct quantum states having the same energy u_k . We can pull out the particular state $j=k$ from the inner sum to yield

$$\langle N_k \rangle = \frac{\sum_{n_j}^m n_k g_k \exp(-n_k u_k / k_B T) \sum_{n_j, j \neq k}^{N-m} \exp\left(-\sum_{j \neq k} n_j u_j / k_B T\right)}{\sum_{n_j}^m \exp(-n_k u_k / k_B T) \sum_{n_j, j \neq k}^{N-m} \exp\left(-\sum_{j \neq k} n_j u_j / k_B T\right)}$$

where the constraint on the first sum over n_k with m particles and the second sum over n_j with $N - m$ particles are correlated so that the total number of particles is still N .

Please note that these mean values can be calculated even more simply using the method of Lagrange multipliers, or other (Legendre-transformed) pdfs [see recommended textbooks for Course: "Thermal Physics" by Kroemer and Kittel, or "Statistical Mechanics" by Reif]. But we persist with the Boltzman formulation here to make a point – the statistical reasoning behind the Boltzman pdf remains correct independent of the particle identity.

Fermi-Dirac and Bose-Einstein Statistics

Because of Pauli exclusion of Fermions, $n_k = 0$ or 1 , and we can sum over $n_k = 0$ or 1 in the first sum to yield

$$\langle N_k \rangle = \frac{g_k \exp(-u_k/k_B T) \sum_{n_j, j \neq k}^{N-1} \exp\left(-\sum_{j \neq k} n_j u_j / k_B T\right)}{\sum_{n_j, j \neq k}^N \exp\left(-\sum_{j \neq k} n_j u_j / k_B T\right) + \exp(-u_k/k_B T) \sum_{n_j, j \neq k}^{N-1} \exp\left(-\sum_{j \neq k} n_j u_j / k_B T\right)}$$

Dividing numerator and denominator by the obvious common factor, we get finally,

$$\langle N_k \rangle = \frac{g_k}{1 + \exp(+u_k/k_B T) \frac{\sum_{n_j, j \neq k}^N \exp\left(-\sum_{j \neq k} n_j u_j / k_B T\right)}{\sum_{n_j, j \neq k}^{N-1} \exp\left(-\sum_{j \neq k} n_j u_j / k_B T\right)}}$$

Asymptotic analysis shows that for large N:

$$\begin{aligned} \frac{\sum_{n_j, j \neq k}^N \exp\left(-\sum_{j \neq k} n_j u_j / k_B T\right)}{\sum_{n_j, j \neq k}^{N-1} \exp\left(-\sum_{j \neq k} n_j u_j / k_B T\right)} &\approx \frac{\exp \sum_{n_j, j \neq k}^N \left(-\sum_{j \neq k} n_j u_j / k_B T\right)}{\exp \sum_{n_j, j \neq k}^{N-1} \left(-\sum_{j \neq k} n_j u_j / k_B T\right)} \equiv \frac{\exp[-u(N)/k_B T]}{\exp[-u(N-1)/k_B T]} \\ &= \exp\left[-(U(N) - U(N-1))/k_B T\right] \end{aligned}$$

where U is the total internal energy of N particles (a macroscopic thermodynamic variable !)

So from 1st law of thermodynamics,

$$U(N + \delta N) = U(N) + \frac{\partial U}{\partial N} \delta N \equiv U(N) + \mu \delta N$$

where μ is the chemical potential (intensive variable), defined as the change in internal energy per unit change in particle number. By change of variable, $N = N' - 1$ and because the smallest $\delta N = 1$ for any particle (by definition), we get

$$U(N' - 1 + 1) = U(N' - 1) + \mu, \text{ or } U(N') - U(N' - 1) = \mu. \text{ Thus we can write,}$$

$$\exp(-(U(N) - U(N-1))/k_B T) = \exp(-\mu/k_B T), \text{ and}$$

$$\langle N_k \rangle = \frac{g_k}{1 + \exp[(U_k - \mu)/k_B T]} \text{ subject to the constraint } \sum_k \langle N_k \rangle = N$$

This is the famous Fermi-Dirac function. From the derivation given here it should be clear that the F-D function is not a distribution function in the usual probabilistic sense. Rather, it is a statistical average taken over the Boltzman pdf under the special constraints of the Pauli

exclusion principle and the requirement that the total number of particles in the system is N . And the final average value, $\langle N_k \rangle$ is the mean number of particles in all quantum states indexed by k having the common energy U_k . The number of distinct k states having this common U_k is the degeneracy factor g_k . As we shall see, it is very convenient to couple the F-D function to quantum mechanics which (through the Schrödinger equation) naturally categorizes the possible quantum states according to distinct quantum states (eigenvectors) and corresponding total energy (eigenvalue). It is a common result that there are several different eigenvectors sharing a common eigenvalue, which is conventionally called the quantum state degeneracy.

By following a similar line of analysis to that given above but applying the combinatorial reasoning for particles of zero or integral spin (bosons), we would note that n_j can have any value from 0 to ∞ , and would end up with the expression

$$\langle N_k \rangle = \frac{g_k}{-1 + \exp[(U_k - \mu)/k_B T]}$$

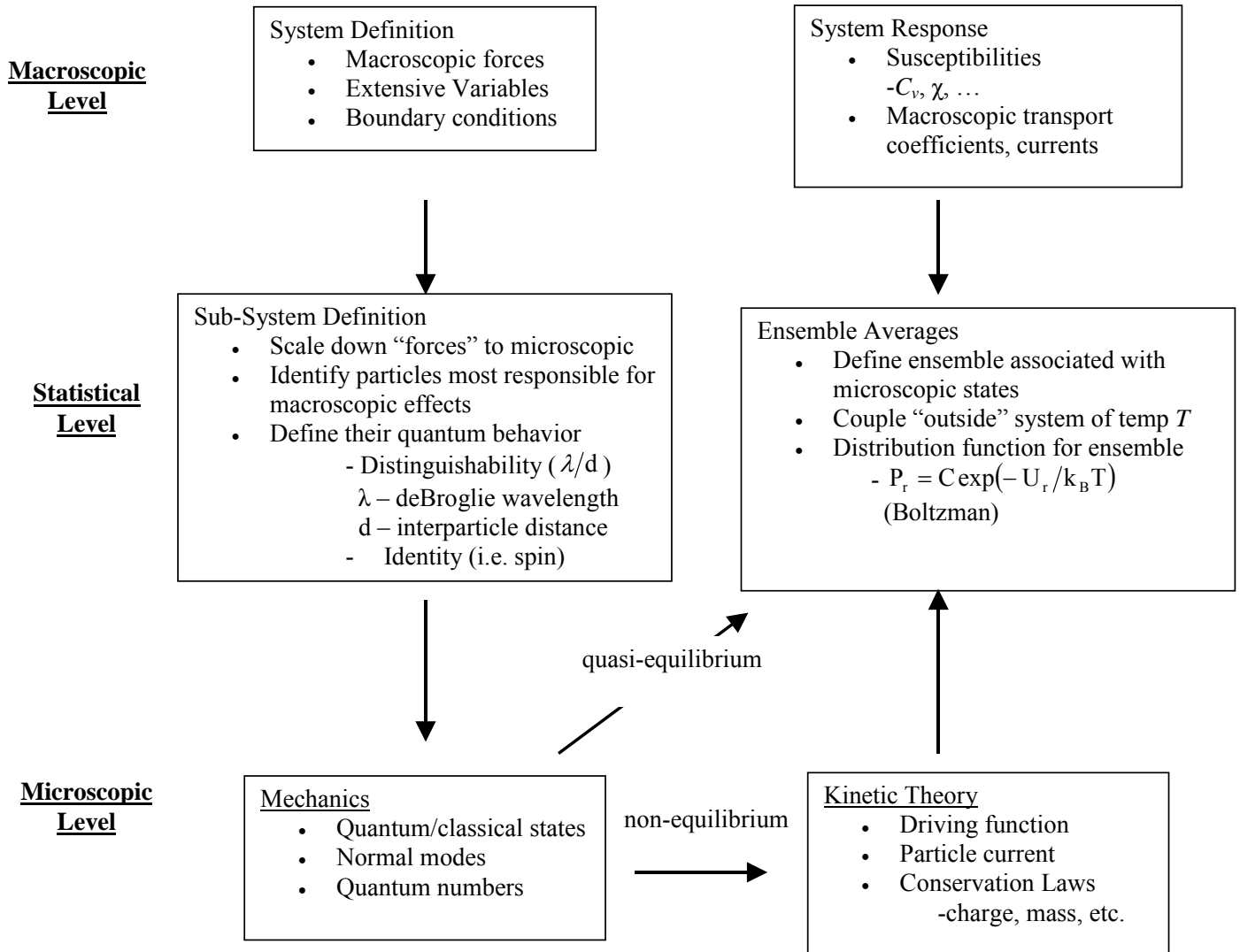
This is the famous Bose-Einstein function, again not a probability distribution function in the usual sense but a mean value of particles in all states having energy U_k . In the special case that the bosons are massless, then the chemical potential vanishes (i.e., massless particles can do no chemical work), and we end up with

$$\langle N_k \rangle = \frac{g_k}{-1 + \exp[(U_k)/k_B T]}$$

This is a special case that applies to photons and phonons, both massless bosons. We will be using it for phonons extensively in this course.

Hierarchy of Solid-State Engineering

The combination of thermodynamics at the macroscopic level, classical or quantum mechanics at the microscopic level, and statistical mechanics to couple them together, leads to a powerful methodology in explaining phenomena in solids and in engineering them for specific purposes. The methodology can be represented by the flowchart shown below that we call the “hierarchy” of solid state. The word “hierarchy” is appropriate because it tends to get followed rather religiously in this course and in the solid-state field as a whole, whether people realize it or not. For students, confusion is often caused by the fact that solid-state analyses often commence somewhere inside the hierarchy, and may or may not complete the loop back to the macroscopic level. In this Course, we will always try to keep track of “where we are” in this flow chart.



Example of Hierarchy: Conduction electrons in a metal

- Equilibrium (electric and magnetic susceptibility) and non-equilibrium (e.g., electrical and thermal conductivity) properties in a metal depend strongly on the conduction electrons. A very important measure of the affect of the electrons on many of these properties is the heat capacity.

$$C_v = \left. \frac{\delta Q}{\delta T} \right|_v = \left. \frac{T dS}{dT} \right|_v = \left. \frac{du}{dT} \right|_{v,N,P,M,\dots}$$

- At microscopic level, we know that each atom contributes approximately one conduction electron and that separation of atoms is approximately 3 \AA

$$\Rightarrow d = 3 \text{ \AA}$$

We also guess (will prove later) that the kinetic energy of typical conduction electron

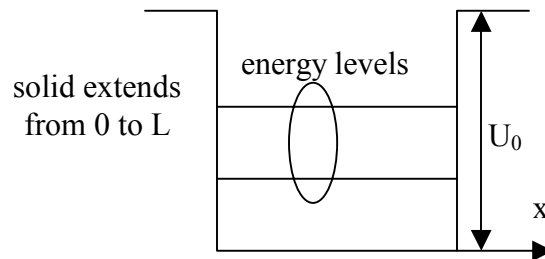
$$U_k \approx 1\text{eV} = \frac{p^2}{2m}$$

$$\Rightarrow p = \sqrt{2mU} \cong 5.4 \times 10^{-25}$$

$$\Rightarrow \lambda_d = h/p \cong 12 \text{ \AA}$$

So $d < \lambda_d =$ and the electrons are indistinguishable and quantum mechanics is required for energy states.

- Quantum mechanics is solved most easily by treating conduction electrons as independent and free particles confined to solid by a "binding energy", U_0 . Let's do 1D only.



Schrödinger equation $\frac{-\hbar^2}{2m} \frac{d^2\psi}{dx^2} + V\psi = U\psi$ where $\hbar = \frac{h}{2\pi}$

\uparrow potential energy \uparrow total energy

Inside solid $V = -U_0$; so let's define $U' = U + U_0$

Get
$$-\frac{\hbar^2}{2m} \frac{d^2\psi}{dx^2} = U'\psi$$

For boundary condition, assume U_0 is large enough that electrons can not leave the solid
 $\Rightarrow \psi(0) = \psi(L) = 0$ Re-writing Schrodinger, we leave

$$\frac{d^2\psi}{dx^2} + \frac{2mU'}{\hbar^2}\psi = 0$$

Solution:
$$\psi = \sin\left(\sqrt{\frac{2mU'}{\hbar^2}}(x)\right)$$

Boundary Condition at $x = 0$ is satisfied trivially

b.c. at $x = L \Rightarrow 0 = \sin\left(\sqrt{\frac{2mU'}{\hbar^2}}(L)\right) \Rightarrow \sqrt{\frac{2mU'}{\hbar^2}}(L) = \pi, 2\pi \dots = n\pi$

We recognize, from wave phenomena, that the quantity $\sqrt{\frac{2mU'}{\hbar^2}}$ has the units of a wave vector, k .

So we define $k \equiv \sqrt{\frac{2mU'}{\hbar^2}}$, and B.C. at $x=L \Rightarrow kL = n\pi$ or $k = \frac{n\pi}{L}$, $n = 1, 2, 3, \dots$

$$U' = \frac{\hbar^2 k^2}{2m} = \frac{1}{2m} \frac{(\hbar n \pi)^2}{L^2}, \quad n = 1, 2, 3, \dots$$

Rather than indexing the energy state of the electron by the classical momentum or velocity, we now do it through the wave vector k or "quantum number" n

- This becomes a general theme in solids: particles that are indistinguishable and independent become indexed by the wave vector (or associated quantum number) of their quantum state (solution to Schrödinger wave equation)
- Particles that are distinguishable but rather strongly interacting can often be analyzed by transforming the interaction away with new (generalized) coordinates. The resulting particles are often massless, independent collective excitations that are indistinguishable, so get a special form of Bose Einstein statistics called photon statistics.

e.g. <u>interacting particles</u>	<u>collective excitation</u>
atomic cores	phonons
atomic spins	magnons

- particles that are indistinguishable and strongly interacting are the most difficult to deal with

- in some cases we can treat them as independent particles with a modified (i.e., "dressed") mass.

In this case, we call the independent particles quasiparticles.

- in other cases we can find new states consisting of strongly-bound interacting particles, rather isolated from the rest (e.g., excitons in wide gap semiconductors, Cooper pairs in superconductors).