In last lecture, we discussed the N-particle distribution function. We have obtained

$$\text{No. Systems} = f^{(N)}\left(t, \mathbf{r}^{(n)}, \mathbf{p}^{(n)}\right) \Delta \mathbf{r}^{(n)} \Delta \mathbf{p}^{(n)}$$

in a small volume of the phase space, $\Delta \mathbf{r}^{(n)} \Delta \mathbf{p}^{(n)}$,
where $\Delta \mathbf{r}^{(n)} = \Delta \mathbf{r}_1 \Delta \mathbf{r}_2 \ldots \Delta \mathbf{r}_N = \Delta r^{(1)} \Delta r^{(2)} \ldots \Delta r^{(n)}$ and $\Delta \mathbf{p}^{(n)} = \Delta \mathbf{p}_1 \Delta \mathbf{p}_2 \ldots \Delta \mathbf{p}_N = \Delta p^{(1)} \Delta p^{(2)} \ldots \Delta p^{(n)}$.
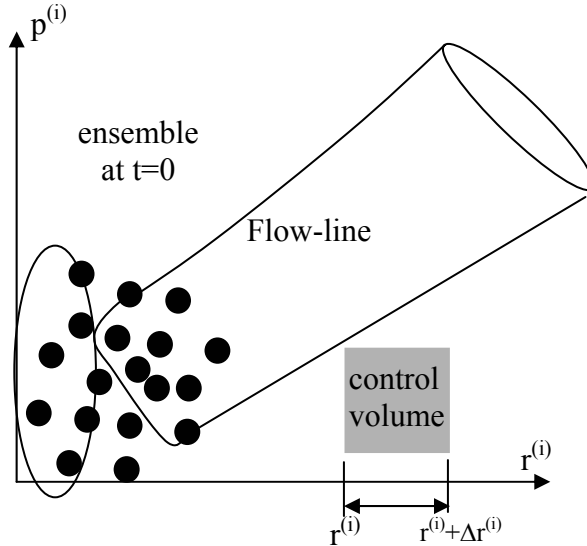
The time evolution of $f^{(N)}(t, \mathbf{r}^{(n)}, \mathbf{p}^{(n)})$ in the phase space is governed by the **Liouville equation**,

$$\frac{\partial f^{(N)}}{\partial t} + \sum_{i=1}^{n} \dot{r}^{(i)} \times \frac{\partial f^{(N)}}{\partial r^{(i)}} + \sum_{i=1}^{n} \dot{p}^{(i)} \times \frac{\partial f^{(N)}}{\partial p^{(i)}} = 0$$

which can be derived based on the fact that the traces of systems in the ensemble do not intersect.

Note: The number of the degree of freedom in the phase space is normally very big. For 3D cases, it is $6N_A = 6 \times 6.02\text{E}23$.

The Liouville equation involves a huge number of variables, which makes its impractical in terms of the boundary and initial conditions, as well as analytical and numerical solutions. One way to simplify the Liouville equation is to consider one particle in a system. This is a representative particle having coordinate $\mathbf{r}_1$ and momentum $\mathbf{p}_1$, each of the vectors has m components, i.e., m-degrees of freedom. We introduce a **one-particle distribution function** by averaging the N-particle distribution function over the rest (N-1) particles in the system,

$$f^{(1)}(t, \mathbf{r}_1, \mathbf{p}_1) = \frac{N!}{(N-1)!} \int \bullet \bullet \bullet \int f^{(N)}(t, \mathbf{r}^{(n)}, \mathbf{p}^{(n)}) d\mathbf{r}_2 \bullet \bullet \bullet d\mathbf{r}_N d\mathbf{p}_2 \bullet \bullet \bullet d\mathbf{p}_N.$$

For simplicity in notation, we will drop the subscript 1 and understand ($\mathbf{r}$,$\mathbf{p}$) as the coordinates and momenta of one particle. Since $f^{(N)}(t, \mathbf{r}^{(n)}, \mathbf{p}^{(n)})$ represents the number density of systems having generalized coordinates ($\mathbf{r}^{(n)}, \mathbf{p}^{(n)}$) in the ensemble, the one particle distribution function represents number density of systems having ($\mathbf{r}$,$\mathbf{p}$),
$f(t, \mathbf{r}, \mathbf{p}) d^3\mathbf{r} d^3\mathbf{p}$ = number of systems in $d^3\mathbf{r} d^3\mathbf{p}$.

With the introduction of the averaging method to obtain the one-particle distribution function, one can start from the Liouville equation and carry out the averaging over the space and momentum coordinates of the other (N-1) particles. This procedure leads to

$$\frac{\partial f}{\partial t} + \frac{d\mathbf{r}}{dt} \bullet \nabla_{\mathbf{r}} f + \frac{d\mathbf{p}}{dt} \bullet \nabla_{\mathbf{p}} f = \left(\frac{\partial f}{\partial t} \right)_c$$

where the subscripts ($\mathbf{r}$ and $\mathbf{p}$) in the gradient operators represent the variables of the gradient. The scattering term $\left(\frac{\partial f}{\partial t} \right)_c$ will be discussed in details later in this lecture. The above equation is the **Boltzmann equation** or Boltzmann transport equation.

Note: The derivative $\frac{d\mathbf{r}}{dt}$ has the meaning of velocity, while $\frac{d\mathbf{p}}{dt}$ denotes force.
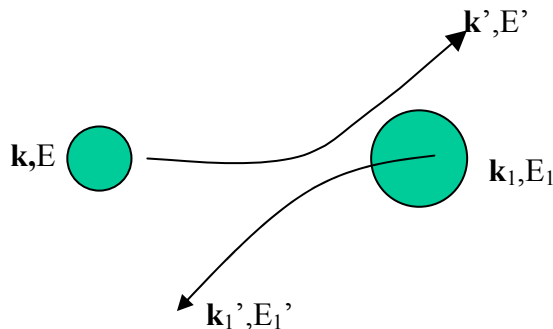
Consider the collision process between two particles as shown in the above figure. After the collision, the energy and the velocity of each particle may change. Clearly, the collision is a time-dependent process. The rigorous way of dealing the collision process is to solve the corresponding time-dependent Schrödinger equation for the combined system made of both particles. This is, however, usually very complicated and not practical. A simpler way to treat the collision is to use the perturbation method. This method considers the time-dependent interaction between the two particles as a small perturbation in energy, H'($\mathbf{r}$,t), from the original steady-state, non-interacting energy H_o of the two particles, such that the total system energy is
$$H = H_o(r) + H'(\mathbf{r}, t),$$
where we have learned that the Hamitonian H_0 is

$$H_0 = \frac{\hat{p}^2}{2m} + U = \frac{1}{2m}\left(-i\hbar\nabla\right)^2 + U = \frac{-\hbar^2}{2m}\nabla^2 + U$$

in the Schrödinger equation $H_0\Psi = E\Psi$.

By treating H' as a small perturbation to unperturbed Hamiltonian H$_o$, the solution of the Schrödinger equation for the new H can be obtained through perturbation method and expressed in terms of the wave functions Ψ of the unperturbed two-particle system with a Hamiltonian H$_o$. Using the perturbation solution, one can calculate the probability for the system jumping from one quantum state Ψ_i to another quantum state Ψ_f, both are accessible quantum states of the original two-particle systems. This rate of this probability is the transition rate,

$$W_i^f\left(\mathbf{k},\mathbf{k'},\mathbf{k}_1,\mathbf{k}_1'\right) = \frac{2\pi}{\hbar}\left[\int \Psi_f^* H'\Psi_i d^3\mathbf{r}\right]^2 \delta\left(E_f - E_i\right)$$

$$= \frac{2\pi}{\hbar}\left|\left\langle i\left|\mathrm{H}'\right|f\right\rangle\right|^2 \delta\left(E_f - E_i\right)$$

$$= \frac{2\pi}{\hbar} M_{if}^2 \delta\left(E_f - E_i\right)$$

where d^3**r**=dxdydz means integration over the whole volume of the system and

$$\mathrm{M_{if}} \equiv \left\langle \mathrm{i}\left|\mathrm{H}'\right|\mathrm{f}\right\rangle \equiv \int \Psi_\mathrm{f}^* \mathrm{H}'\Psi_\mathrm{i} \mathrm{d}^3\mathbf{r}$$

is called the scattering matrix. The Kronecker delta function, $\delta(\mathrm{E_f - E_i})$, implies that the energy must be conserved in the process. This equation is one form of the often-referred **Fermi golden rule**.

The scattering term in the Boltzmann equation is the net gain of particles in one quantum state. This net gain consists of two components: one is the increase of the number of particles due to scattering from other quantum states into the quantum state under consideration. The other is the decrease of the number of particles due to scattering from the current quantum states to other quantum states. We again take two-particle scattering process as an example. The initial wave vector of the particle is **k** and it collides with a particle with a wavevector $\mathbf{k}_1$. The corresponding distribution functions for the two particles are f(t,**r**,**k**,t) and f(t,$\mathbf{r}_1$,$\mathbf{k}_1$). After scattering, the momentum of the two particles are **k'** and $\mathbf{k}_1'$ and their distribution functions are f(**r'**,**k'**,t) and f($\mathbf{r}_1'$,$\mathbf{k}_1'$,t), respectively. The scattering term for the particle at state **k** can be expressed as

$$\left(\frac{\partial f}{\partial t}\right)_c = -\int f\left(\mathbf{r},\mathbf{k},t\right)f\left(\mathbf{r},\mathbf{k}_1,t\right)W\left(\mathbf{k},\mathbf{k}_1 \rightarrow \mathbf{k'},\mathbf{k}_1'\right)d^3\mathbf{k}_1 d^3\mathbf{k'}d^3\mathbf{k}_1'$$

$$+\int f\left(\mathbf{r},\mathbf{k'},t\right)f\left(\mathbf{r},\mathbf{k}_1',t\right)W\left(\mathbf{k'},\mathbf{k}_1' \rightarrow \mathbf{k},\mathbf{k}_1\right)d^3\mathbf{k}_1 d^3\mathbf{k'}d^3\mathbf{k}_1',$$

where the first term on the right hand side represents the rate of particles being scattered out of quantum states determined by **k** and $\mathbf{k}_1$, and the second term represents rate of particles scattered into the quantum state.

When discussing the interfacial thermal conductance in Lecture 14, we have obtained $q_{1\rightarrow2}\left(T_{e2}\right) = q_{2\rightarrow1}\left(T_{e2}\right)$ by considering the equilibrium status q_{12}=0 and T_{e2}=T_{e1}. Based on

a similar argument, the above equation can be simplified by noticing in the equilibrium status

$$W\left(\mathbf{k},\mathbf{k}_1 \rightarrow \mathbf{k}',\mathbf{k}_1'\right)=W\left(\mathbf{k}',\mathbf{k}_1' \rightarrow \mathbf{k},\mathbf{k}_1\right).$$

This leads to

$$\left(\frac{\partial f}{\partial t}\right)_c = -\frac{V^3}{(2\pi)^9}\int W\left(\mathbf{k},\mathbf{k}_1 \rightarrow \mathbf{k}',\mathbf{k}_1'\right)\left[f\left(\mathbf{r},\mathbf{k},t\right)f\left(\mathbf{r},\mathbf{k}_1,t\right)-f\left(\mathbf{r},\mathbf{k}',t\right)f\left(\mathbf{r},\mathbf{k}_1',t\right)\right]d^3\mathbf{k}_1 d^3\mathbf{k}' d^3\mathbf{k}_1'$$

where the factor $\dfrac{V^3}{(2\pi)^9}$ appears in the conversion from summation over wavevector into

integration over the phase space.

The integral-differential Boltzman equation is very difficult to solve in general. Most solutions rely on a drastic simplification of the scattering integral by the relaxation time approximation,

$$\left(\frac{\partial f}{\partial t}\right)_c = -\frac{f-f_o\left(T,E,\mu\right)}{\tau\left(\mathbf{r},\mathbf{k}\right)},$$

where $\tau(\mathbf{r},\mathbf{k})$ is the **relaxation time**, and f_o represents the equilibrium distribution of the carriers, such as the Boltzmann, the Fermi-Dirac, and the Bose-Einstein distributions given in chapter 4. Under the relaxation time approximation, the Boltzmann equation becomes

$$\frac{\partial f}{\partial t}+\mathbf{v}\bullet\nabla_{\mathbf{r}}f+\frac{\mathbf{F}}{m}\bullet\nabla_{\mathbf{v}}f=-\frac{f-f_o}{\tau}.$$

Note: In fluid mechanics, we have a counterpart of the Boltzmann equation, which is called the Krook equation.
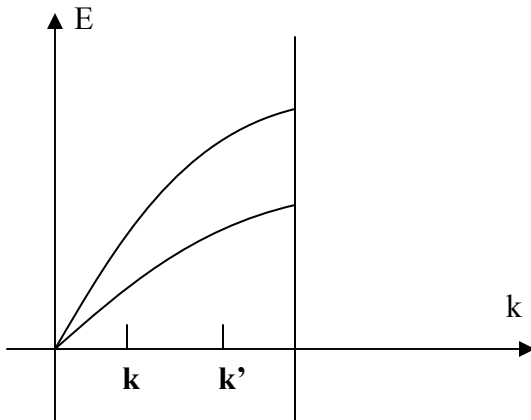
Now let us consider the general rules of the phonon-phonon scattering. First we have energy balance as

$$E_f = E_i \Rightarrow E\left(\mathbf{k}_1\right)+E\left(\mathbf{k}\right)=E\left(\mathbf{k}_1'\right)+E\left(\mathbf{k}'\right).$$

Secondly we have momentum conservation

$$\mathbf{G}+\mathbf{k}_1+\mathbf{k}=\mathbf{k}_1'+\mathbf{k}',$$

where the vector **G** accounts for the momentum imbalance between the initial and final states when $|\mathbf{k}_1 + \mathbf{k}| > \pi/a$. We have learned that $|\mathbf{k}_1 + \mathbf{k}| > \pi/a$ (out of the first Brillouin zone) is meaningless and must be flipped over into the first Brillouin zone. This momentum difference is compensated by **G**. We call this process umklapp process. In other case, **G**=0 and it is called a normal process.


(a)   (b)
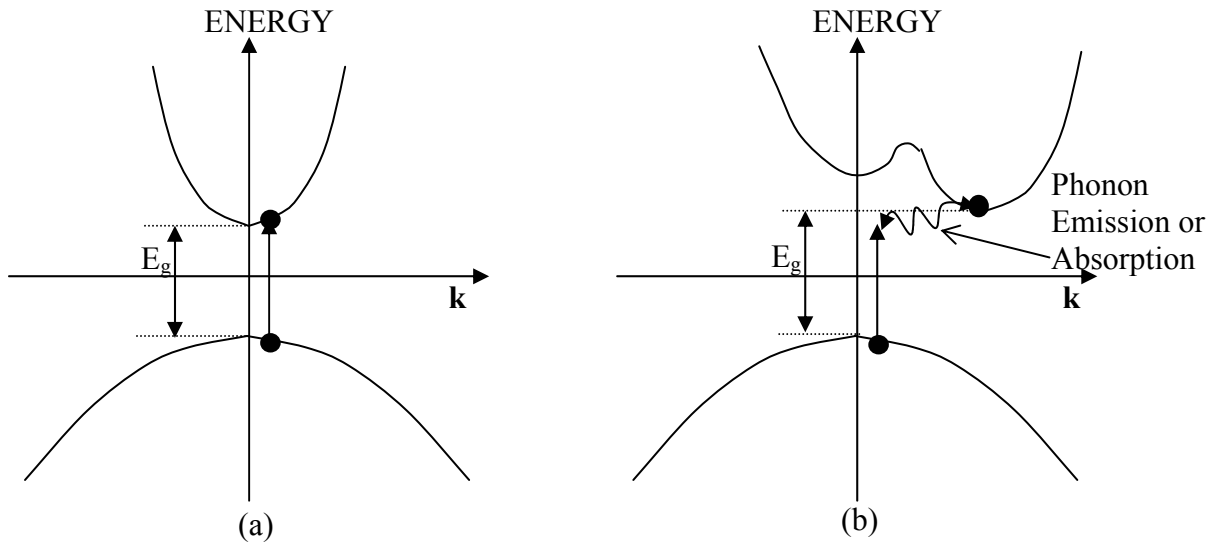
The absorption of photons by free electrons in metals and in semiconductors must be accompanied by emission or absorption of phonons because of momentum conservation. In the above figures, figure (a) shows that an electron absorbs a photon and is pumped to a different band (direct semiconductor). We still have

$E_i + \hbar\omega = E_f$ (energy conservation)

$\mathbf{k_i} + \dfrac{h}{\lambda} = \mathbf{k_f}$ (momentum conservation),

where $\dfrac{h}{\lambda}$ is the photon momentum and can be proved to be negligible for optical lights ($\lambda \sim 0.5 \ \mu m$). Therefore, the arrow points upward almost vertically.
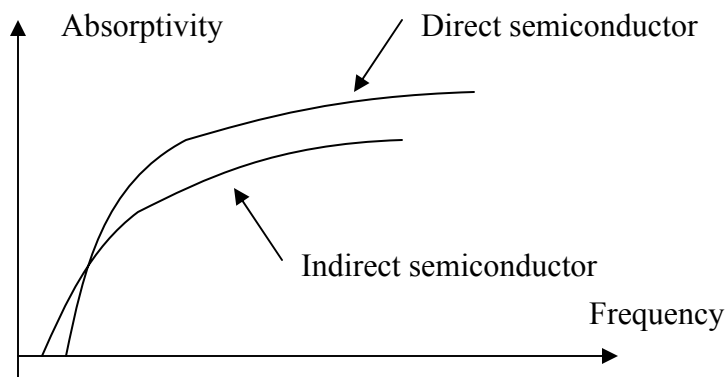
For silicon (indirect semiconductor), we have the situation drawn in figure (b). In this case, the absorption of a photon cannot happen at the band edge without the absorption or emission of phonons because photon-electron interaction alone does not satisfy the wave vector conservation requirements. The participation of phonons in the process reduces the absorption or emission of photons, as shown in the above figure.

Generally speaking, electrons will collide with electrons, phonons, and impurities in the crystals. For a normal process in which two phonons merge into one (shown in the figure below), both the energy and momentum are conserved and will not create any thermal resistance to the heat conduction. In fact, the finite thermal conductivity of a crystal results from the random umklapp process with compensating **G**. It has the relaxation time

$$\tau_u^{-1} = Be^{-\theta_D / bT} T^3 \omega^2$$

.
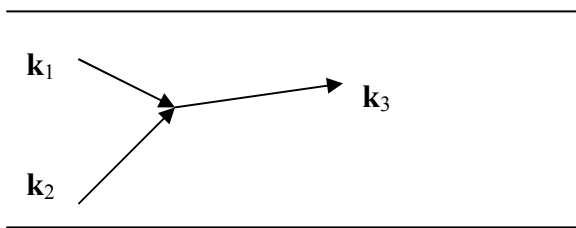
For impurity scattering, we have the familiar Rayleigh law

$$\tau_I^{-1} = A\omega^4 .$$

Note the scattering possibility is proportional to the reciprocal of relaxation time. This equation suggests that the scattering is enhanced for increased ω.

Note: (1) Normally we assume the size of defects $d \ll \lambda$. (2) The blue sky is the result of impurity scattering that shields off the high frequency lights.

The total relaxation time is obtained by combining the expressions for individual relaxation processes according to the Mathiessen rule

$$\frac{1}{\tau} = \sum \frac{1}{\tau_j} ,$$

which is used in the expression of $\dfrac{f - f_o}{\tau}$.

For phonon scattering, the two-particle collision is drawn as following.
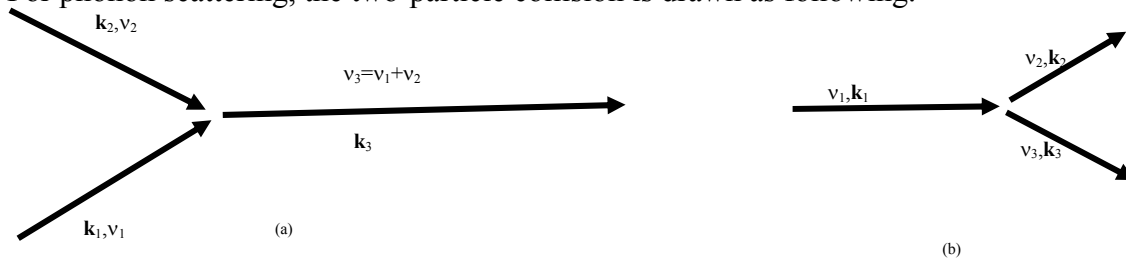
For the merging of two phonons into one, the energy conservation gives
$$h\nu_1 + h\nu_2 = h\nu_3$$
and a similar equation can be written for the process that one phonon splits into two. The momentum conservation during the three-phonon interaction processes takes a special form. For the phonon merging process, the momentum conservation can be written as

$$\mathbf{k}_1 + \mathbf{k}_2 = \mathbf{k}_3 + \mathbf{G}$$

where the reciprocal lattice vector $\mathbf{G}$ can be zero or a linear combination of the reciprocal lattice vectors. If $(\mathbf{k}_1 + \mathbf{k}_2)$ is smaller than the first Brillouin zone wavevector, $\mathbf{G}$ equals $\mathbf{0}$, otherwise, $\mathbf{G} \neq \mathbf{0}$. This comes from the requirement that the phonon wavelength cannot be smaller than the lattice constant as we discussed in chapter 3. The $\mathbf{G}=\mathbf{0}$ phonon scattering process is called the **normal process** and the $\mathbf{G} \neq \mathbf{0}$ is the **umklapp process**, as mentioned before.
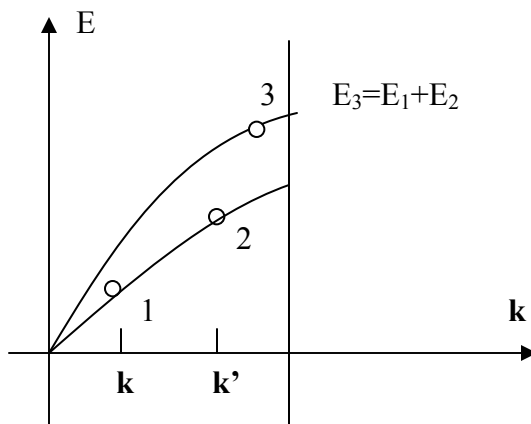
Note: In the perturbation method, we consider the time-dependent interaction between the two particles as a small perturbation in energy, H'($\mathbf{r}$,t). When we use the harmonic oscillator approximation for the actual interatomic potentials, the higher order term $O[(x'-x_o)^3]$ in

$$U(x') = U(x_o) + \frac{1}{2}\left[\frac{d^2U}{dx'^2}\right]_{x'=x_o} (x'-x_o)^2 + O\!\left[(x'-x_o)^3\right]$$

can be considered as the perturbation from the harmonic potential. In the umklapp process, the randomly distributed vector $\mathbf{G}$ plays a similar role as $O[(x'-x_o)^3]$.
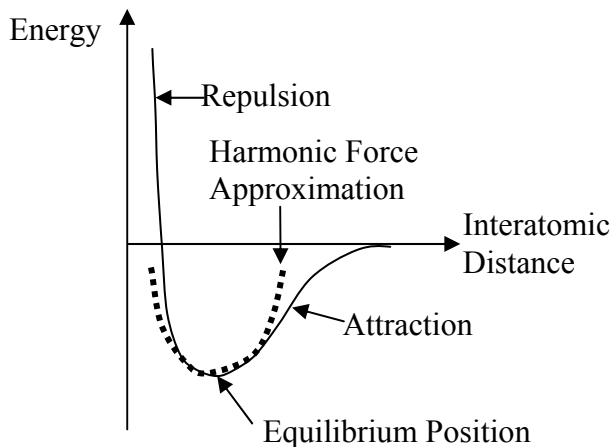
When the particles have a nonzero average velocity **u**, the following **displaced Maxwell velocity distribution** is often used for f_0

$$f_o(\mathbf{v}) = n\left(\frac{m}{2\pi\kappa_B T}\right)^{3/2} e^{-m\left[(\mathbf{v}-\mathbf{u})^2\right]/2\kappa_B T},$$

where **u** can change at different location in the space.

If the solution of the Boltzmann equation is known for a problem, we can calculate the volume-average of any microscopic property X of the particle from,

$$\langle X(\mathbf{r})\rangle = \frac{1}{V}\sum_{\mathbf{k},s} X(\mathbf{r},\mathbf{k})f,$$

where the summation can be conducted over wave vector **k** or velocity **v**.

Assumption of the Boltzmann equation
  (1) The Boltzmann equation is only applicable to diluted systems, such as phonons, electrons, molecules, and photons. It can never be used for liquids.
  (2) Consider the collision of two particles. Before and after the collision, the distribution functions of the one of the two particles are independent of the coordinates and momentum of the other particle. This is the so called the **molecular chaos** assumption. Additionally, the particles have no memory of its history and its final state is unaffected by its very beginning status.
  (3) The Boltzmann equation cannot include explicitly the wave effects such as interference and tunneling. We use the particle picture for all particles though photons have larger wavelength and is more like a wave. The wave theory is partially included for some problems. For example, we have solved the wavefunctions of electrons in deriving the band structure in crystals. The wavelength is far larger than the interatomic distance.