Chapter 4.

THE STRUCTURE OF ATOMIC AND MOLECLAR ENSEMBLES

4.1. Intermolecular interactions

The molecular ensembles can be studied according to different points of view.

The *phenomenologic method* regards the system as homogeneous, and describes it with pure macroscopic parameters. This is the thermodynamic mode of discussion.

The *molecular method* regarded the system as a heap of molecules and describes the system with the properties of the molecules and their interactions. This is the molecular mechanical (dynamical or statical) mode.

4.1.1. The theoretical description of the intermolecular interactions

The intermolecular interactions can be regarded in good approach as the result of several interactions. The *energy of interactions* (E_{ia}) is the difference of total energy of the system (E) and the sum of the energies of the isolated molecules (E_i).

$$E_{ia} = E - \sum_{i=1}^{N} E_i \tag{4.1}$$

N is the number of the molecules in the heap.

The energy of interaction can be partitioned into interaction between molecular pairs, triplets, quadruplets etc.

$$E_{ia} = \sum_{i=1}^{N} \sum_{j=i+1}^{N} E_{ij} + \sum_{i=1}^{N} \sum_{j=i+1}^{N} \sum_{k=j+1}^{N} E_{ijk} + \ldots + E_{i,j,k,\ldots,N} \tag{4.2}$$

The dominating interactions are the *pair interactions*.

$$E_{ia} = \sum_{i=1}^{N} \sum_{j=i+1}^{N} E_{ij} \tag{4.3}$$

The Hamilton operator of a bimolecular interacting system is

$$\hat{H}_{ij} = \hat{H}_i + \hat{H}_j + \hat{V} = \hat{H}^0 + \hat{V} \tag{4.4}$$

The zero superscript refers on the state without interactions. $\hat{V}$ is the operator of the intermolecular potential energy describing the interactions with the electrons and nuclei of the other molecule. Let φ_I the eigenfunction of the isolated molecule i, φ_j the same of the isolated molecule j.

$$E_{ij} = \int \varphi_j^* \varphi_i^* \hat{V} \varphi_i \varphi_j d\tau \tag{4.5}$$

is the interaction energy between the two molecules. If the overlap of the wavefunctions of the two molecules is not very large E_{ij} can devided into first order and second order perturbations

$$E_{ij} = E_{ij}^{1} + E_{ij}^{2} \tag{4.6}$$

In case of *first order perturbation* it is supposed that the structure and the charge distribution do not change during the interaction. E_{ij}^{1} can be expressed as function of the multipole moments.

The definition the moments of the of the i-th molecule

$$Q_{i}^{lm} = \frac{4\pi}{2l+1}\left[\sum_{\alpha=1}^{N_j} Z_{\alpha} r_{i\alpha}^{l} Y_{m}^{l}(\vartheta_{i\alpha}, \varphi_{i\alpha}) - \int \rho_j(r_j) r_j Y_{m}^{l}(\vartheta_j, \varphi_j) dr_j\right] \tag{4.7}$$

r,φ and polar coordinates, charges are labeled with z, Y_{m}^{l} is a spheric function, ρ is the charge distribution function of the molecule. The spheric function is the eigenfuntion of the squared orbital momentum operator (the eigenvalues are $l(l+1)$). In Eq. 4.7 l determines the order of the moment. If l=1, this is dipole moment, if l=2, this is quadrupole moment, if l=3, this is octopole moment, etc.

The interaction between charges and moments is proportional to a power of 1/R, R is the distance between the origins of the polar coordinate functions of the two molecules.

Table 4.1. Charge dipole interactions

l_i	l_j	i	j	Power of 1/R
0	0	ion	ion	1
0	1	ion	dipole	2
0	2	ion	quadrupole	3
1	1	dipole	dipole	3
1	2	dipole	quadrupole	4
2	2	quadrupole	quadrupole	5

The quadrupole moment characterizes the asymmetry of the charge distribution in the molecule, i.e. the energies of the various first order perturbations can be expressed according to the the powers of 1/R.

Second order perturbations are those if at least one of the interacting molecules (j) has neither charge nor dipole moment. If molecule i has charge or dipole moment, its electric field induces charges in molecule j. The induced dipole moment is determined by the polarizability α_j. This inductive interaction is proportional to $1/R^4$, to α_j and to the square of the i generated electric field at molecule j.

If both i and j have neither charge nor dipole moment intermolecular interaction can be observed even in this case. This is the *dispersional interaction.* The source of this kind interaction is the time depending charge distribution in the molecules, which is only in time average zero. The energy of the interaction between temporary dipoles in proportional to $1/R^6$, for the dipole-quadrupole it is proportional to $/R^8$ and for quadrupole-quadrupole interactions the proportionality factor is $1/R^{10}$. There for the energy of the second order perturbation can be expessed like

$$E_{ij}^2 = -\frac{C_4^{ij}}{R^4} - \frac{C_6^{ij}}{R^6} - \frac{C_8^{ij}}{R^8} - \frac{C_{10}^{ij}}{R^{10}} \tag{4.8}$$

The *hydrogen bond* is a special interaction. It is weaker then the chemical bond but stronger than the moment – moment interactions. It takes place if the hydrogen atom id bonded to an electronegative atom (movable hydrogen) ant there is in the vicinity an other electronegative atom. Such kind interaction is observable e.g. between two ethanol molecules. The H atom of the OH group of one ethanol molecule builds hydrogen bond with the O of the HO group of the other ethanol molecule. $1/R^{10}$ or $1/R^{12}$ distance dependence is supposed for hydrogen bonds. The hydrogen bond energies are between 10 and 50 kJ/mol. The potential energy function of the hydrogen bond is asymmetric. Fig. 4.1 shows the potential energy function if an NH…O hydrogen bond. The function has two minima, i.e. both in the vicinity of N and O is a minimum, respectively. This curve is similar to that of the large amplitude motions (Subsection 3.5.7). Here is also possible the quantum mechanical tunnel effect. The absolute minimum is close to the N atom, the N-H distance is 102.9 pm, the energy barrier is 142.1 kJ/mol. The other minimum, the H…O distance is 194.3 pm, the energy barrier is 61.0 kJ/mol.

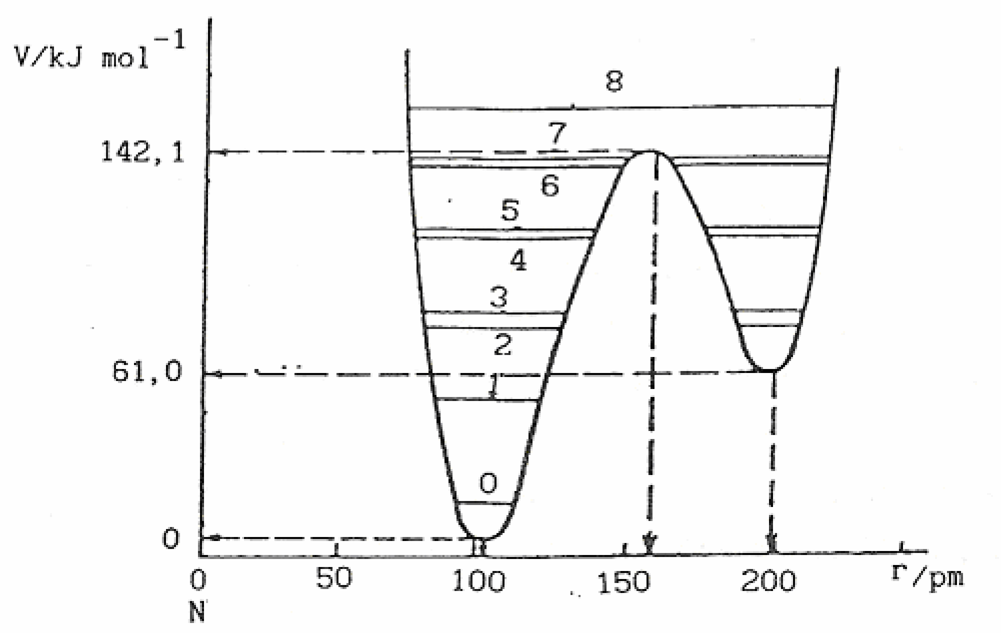

Fig. 4.1

4.1.2 The types of intermolecular interactions

The classification of the intermolecular interactions is possible according to their range. Three groups can be distinguished, short range, medium range and long range interactions (Fig. 4.2). The van der Waals radii of the atoms are labeled on this figure by ρ. The van der Waals radius is the radius of the imagined sphere in which other atomic spheres cannot penetrate, with the exclusion of the chemical bonds. The name of this radius is in connection with the b constant of the van der Waals state equation. Some values of van der Waals radii, ρ_H=110 pm, ρ_N=150 pm, ρ_O=140 pm, ρ_F=135 pm, ρ_{Cl}=180 pm.

Short range interactions. Their range is shorter than the van der Waals radius. They are mostly very strong or strong interactions,

- chemical bond,
- so-called exchanged repulsion (see Quantum Chemistry),
- charge transfer (Subsection 3.6.2),
- hydrogen bond.

Medium range interactions. Their range is between one and three van der Waals radii units The listed ones can be also weak interactions.

- so-called exchanged repulsion also in this range (see Quantum Chemistry),
- charge transfer, also in this range (Subsection 3.6.2),
- overlapping interactions (overlap of molecular orbitals),
- electrostatic interactions,
- dipole-dipole interactions.

Long range interactions. Their range is over three van der Waals radii units. They are weak or very weak interactions, and are called also van der Waals interactions,

- induced dipole-dipole interactions
- dispersion interactions,
- multipole-multipole interactions.

The medium range interactions are important since the potential energy curve has its minimum in this region (Fig. 4.2).

The greater part of this intermolecular interaction may appear also like *intramolecular interactions* under the partial charges, polar groups, electrodonor and electroacceptor groups of the molecule.

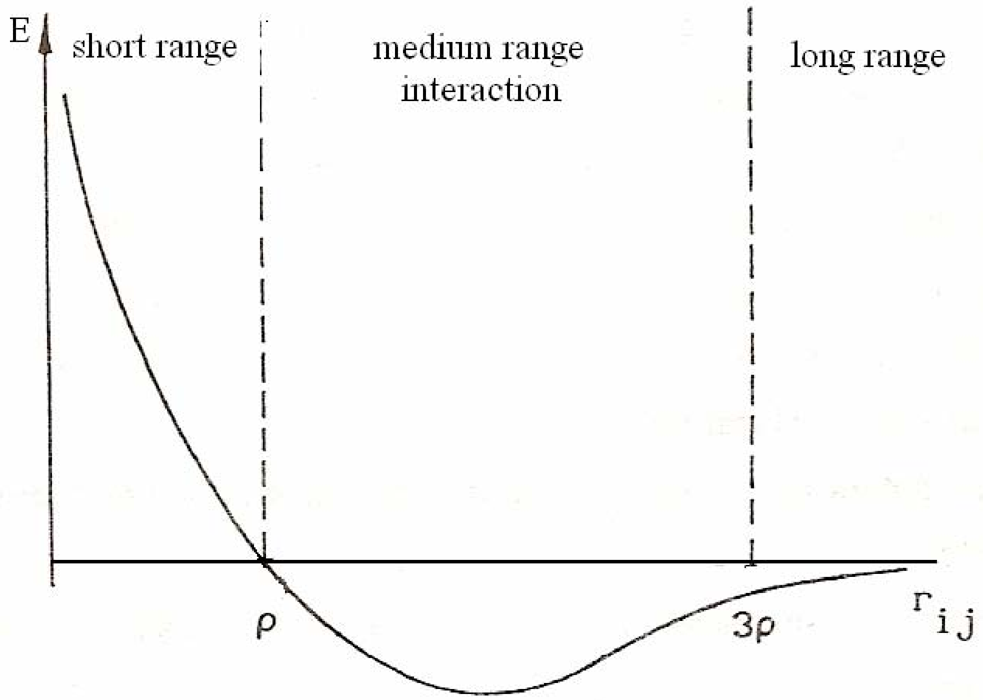

Fig. 4.2

4.2. The structure of molecular ensembles

One cannot speak about structure in *gas phase,* since the structure assumes some ordered state. Of course, there is possible an intermolecular hydrogen bond also in gas phase. There may exist also collision complexes with very short lifetime. Therefore the gas phase is out of the scope of this section.

The *liquid state* show some organization that is a transition state between the gas and the solid states.

In *solid state* one can find a well ordered structure. This structure is sometimes a little distorted by the defects of the crystal lattice. Some solid state materials have high viscosity and are frozen liquids, like glass.

A very important “phase” is the *surface phase* of the phases. The forces acting on the molecules on the surface of a phase are unbalanced since the forces from one phase are stronger than those from the other phase. This is the reason of the surface phase phenomena like adsorption of surface tension.

4.2.1. Liquid state models

Colloids and very viscose liquids are not subjects of this subsection.

Statistical models. This is an attempt to describe the physical properties of liquids based on the properties of the isolated molecules and the intermolecular interactions. Several model ensembles are investigated,

- *microcanonic* ensembles, where the number of particles, the volume and the free energy are constant;
- *canonic* ensembles, where the number of particles, the volume and the temperature is constant;
- *isotherm-isobar ensembles*, where the number of particles, the temperature and the pressure are constant;
- *large canonic ensembles*, where the chemical potential, the volume and the temperature are constant..

The models are built on computers with mathematical methods (programs). The intermolecular interactions are considered by pair potentials. The pair potentials are results of quantum chemical calculations. A potential function is assumed, e.g. exponential function of the intermolecular distance.

The *Monte Carlo methods* choose different states from the particle heap according to Boltzmann's velocity distribution law. Considering the capacity of the computers the simulation calculations can regard only molecular ensembles of some thousand or some ten thousand molecules. Neverttheless, these models are good approaches of the real systems.

The usual way of the choice of the states of the molecular ensembles is the following. Let E_j the internal energy of a distribution (configuration) labeled with j and let this the n-th step during the realization of the state with minimal energy. The n+1-th step is: a molecule will chosen accidentally. This molecule will moved from the P(x,y,z) place to the P(x+u,y+v,z+w) place and we have a new configuration, k. The displacements u, v and w are chosen occasionally from a small (-δ,+δ) region. If E_k<Ej than the new state is k. If E_k>Ej, then it is necessary to calculate the $\exp\left(-\frac{E_k-E_j}{kT}\right)$ expression and compare it with an occasionally chosen number of the [0,1] region. If the chosen number is the greater, the new state will be j, otherwise k. This choice makes possible to come out from a local minima and find the absolute minimum.

This procedure will be repeated until the energy arrives the equilibrium value and begins to oscillate around it. With the averaging of these states several time-independent liquid properties (entropy, free energy, pressure) can be calculated. The results are for short range interactions exact.

The essence of the *molecular dynamic methods* is the following. All particle become a start energy according to the supposed temperature and according to Boltzmann's velocity ditribution law.

The system will be investigated from beginning in ΔT periods. The new coordinates are calculated with the help of the initial velocities. This procedure will be continued until the system arrives the thermal equilibrium. This method gives possibility for determining the time-depending properties of the system.

In the frame of the *supermolecule method* the environment of the molecule is studied. The studied molecule is surrounded with its own or solvent molecules. This is the supermolecule. The properties of the supermolcule are calculable with quantum chemical methods. During the next step the environment of the supermolecule is considered. Regarding the environment of discrete particles pair potentials can be calculated, or regarding it as continuum, that can be characterized by its permittivity. Some quantum chemical methods are based on this view.

For neat liquids the statistical models are preferred, for solutions the supermolecule model seems more successful.

4.2.2 The structure of liquids

The intermoleculare forces are in liquid state essentially greater than in gas phase. Intermolecular connections of different strength may occur from the weakest dispersion ones up to the strongest hydrogen bonds. As consequence of the thermal motion of the molecules some connections break time by time and new ones build. The stronger the connection the smaller the probability of its break. Therefore the liquids are locally ordered.

If the kinetic energy of the compound is high enough, it can leave the liquid phase into the gas phase.

The density of the liquid depends besides the molecular masses also on the intermolecular interactions, since they decrease the intermolecular distances.

If there exist larger ordered parts in the liquid, these can be remain together during the vaporization. They increases the viscosity of the liquids, like also the polymers molecules with high molcular mass.

Cooling the liquid, approaching the melting point, these ordered parts have more and more longer lifetime.

The *liquid crystals* are oritented ordered parts in the liquid, in general they are close to their melting point. This kind liquid is anisotrope (e.g. optically bifringend) in a transient state between the ordered crystal phase and the isotrope liquid. A such kind phase is called *metamophous*. Molecules having long chains are susceptible to build this kind phase. Their long chains build bundles. In case if these bundles are *fixed*, the liquid crytal is *smectic*. During flowing, the bundles glides on one another, therefore the viscosity is high.

If the molecules can glide within the bundle in direction of their long axes, the liquid crystal is *nematic.* An external field orients the nematic phase, the bundles turn into the direction of the external electric field,.Several computer and TV screens are prepated from nematic liquid crystals.

4.2.3. The solide crystalline phase

The crystals are classified from the viewpoint of chemistry according to the sort of the chemical bonds. The *ionic crystals* are kept together by electrostatic forces, while covalent bonds keep together the *atomic crystals*. The forces keeping together the *molecular crystals* are different but weaker, like hydrogen bond, dipole-dipole interactions, dispersion forces. A collective covalent bond, the metallic bond keeps together the *metals*. It is a bond between all the positively charged nuclei and the practically free negative electrons.

The crystalline solid is characterized theoretically by its total order, practically near total order. The crystal is built from elementary cells, *unit cells* those are repeated in all three directions of the space. The symmetry of the crystals differs from that of the molecule.

The symmetry operation of the crystals build *space groups.* Beside the symmetry operations of the point groups (see Subsection 3.1.2) they contain for the description of the periodicity also the special symmetry operations,

- the *srew axis* (C_n^s) is the combination of translation with rotation (Fig. 4.3a);
- the *glide plane* (σ^g) is th combination of translation and reflection (Fig. 4.3b).

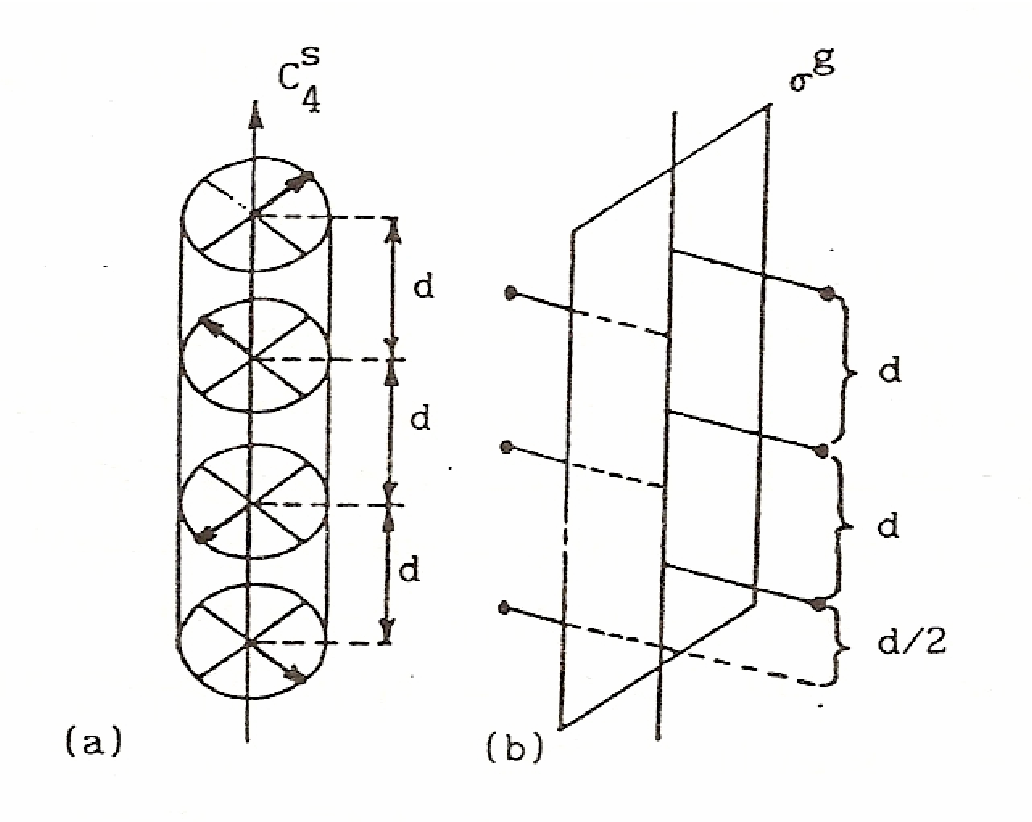

Fig. 4.3

The unit cell may be (Fig. 4.4)

- primitive cell (P), atoms on all corners of a cube;
- base side centered (C), atom are on all corners and in the center of two opposite sides;
- space centered (I), atoms on all corners and in the geometric center of the unit cell;
- side centered (F), atoms on all corners and in the centers of all sides.

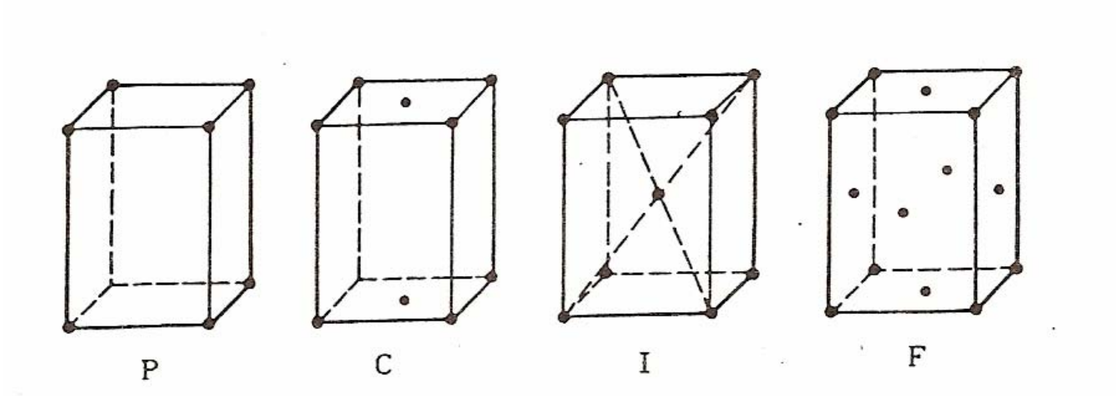

Fig. 4.4

According to the angles between the unit cell axis, relative lengths and number of the axes there exist seven *crystal systems*,

- the triclinic, all angles between the axes are different from one another and from 90^o's,
- the monoclinic, where two axes are perpendicular to one another, the axes are of different length,

- the rhombic, where all the axes are perpendicular to one another but of different lengths,
- the tetragonal, where the axes are perpendicular to one another and two of them are of the same lengths,
- the hexagonal and the trigonal, where the three axes of the four are of the same lengths in the same plane all their interaxial axes are 60^0, the fourth is perpendicular to this plane and is of different length. However, in the trigonal the symmetry of the crystals is trigonal, while in the hexagonal one the symmetry of the crystals is hexagonal,
- the cubic, where all the three axes are perpendicular to one another and the axes are of the same lengths.

The combination of the crystal systems and the unit cell type resulted 32 crystal classes. The combination of the *crystal classes* with the srew axis and glide plane operations led to 240 *space groups*.

It is possible that a unit call contains more than one molecules. These molecules cannot have the same energy levels according to Pauli's exclusion principle. This fact can be observed in the vibrational spectra of the crystal as band splitting.

The crystal is built from unit cells of equivalent structure. Therefore as result of the transformation every atom is transformed into an atom of the same position, so-called *situs*. The atoms of same situs build a *crystal lattice*. The distances of the atoms in the same situs are the *lattice constants*. A three dimensional crystal has three lattice constants.

The crystal planes are determined by *Miller indices.* The positions of the lattice planes relatively to the coordinate axes of the unite cells are determined with these indices. The sides of the unit cells P (Fig. 4.4) crosses perpendicularly only one axis. Therefore their Miller indices are (100), (010) and (001), respectively. This numbers are the reciprocals of the crossing distances, if the cut part of the axis is regarded as unit. If the side does not cross an axes, then the corresponding index is $\frac{1}{\infty} = 0$. The Miller indices are labeled in general with (hkl).

4.2.4 Conductors, semiconductors and insulators in solid state

Our model is in this subsection the crystal lattice of identical atoms, however the results are sometimes applicable also for molecular and ionic crystals.

Let us investigate the state of an electron in a crystal! Two extreme situations are possible:

- the atomic cores are very far from the one another, there is not interaction between them, the electron belongs to the free atom (molecule);
- the electron moves free, the atomic cores do not disturb their motions practically.

The last case defines the *free electron model*. Here the potential energy of the electrons is zero (V=0). The Schrödinger equation of the free electron in a one-dimensional crystal lattice (direction x) (Fig. 4.5)

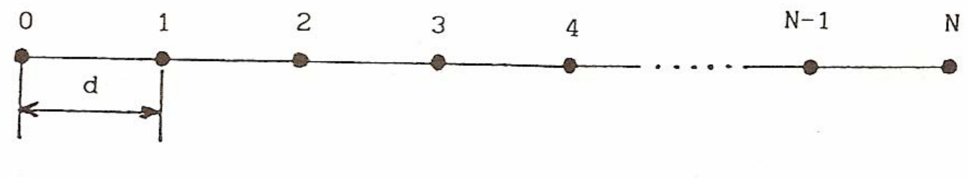

Fig. 4.5

$$-\frac{\hbar^2}{2m_e}\frac{d^2\psi}{dx^2} = E\psi \tag{4.9}$$

Regarding the crystal lattice as symmetrical,

$$\psi(0) = \psi(N)$$

The form of the eigenfunctions is

$$\psi_k(x) = \exp(ikx) \tag{4.10}$$

where the wavenumber vector is

$$k = \frac{2\pi}{N} \qquad \kappa = o, \pm 1, \pm 2, \ldots$$

The energy eigenvalues are

$$E_k = \frac{k^2\hbar^2}{2m_2} \tag{4.11}$$

E_k is the kinetic energy, and the denominator is the square of the particle pulse,

$$I = hk = \frac{\kappa}{N}h = \frac{h}{\lambda} \tag{4.12}$$

If k>0, the electron moves in direction of increasing serial number, otherwise in direction of decreasing one.

If the temperature is 0 K, all electrons are found at the lowest energy level. Since the +k and –k levels are degenerated, at one level two electrons have place with opposite spin. The highest occupied energy level at 0 K is called *Fermi level* (Fig. 4.6a).

Inceasing the temperature, the distribution of the electrons changes. For particles with half spin the Fermi-Dirac ditribution describes their distribution,

$$N = N_F \frac{2}{1 + exp\left(\frac{E - E_F}{kT}\right)} \tag{4.13}$$

N_F is the number of particles on the Fermi level (Fig. 4.6b), E_F is the Fermi level energy. Under electric voltage the particles move away in direction determined by the voltage (on Fig. 4.6c in direction of increasing k).

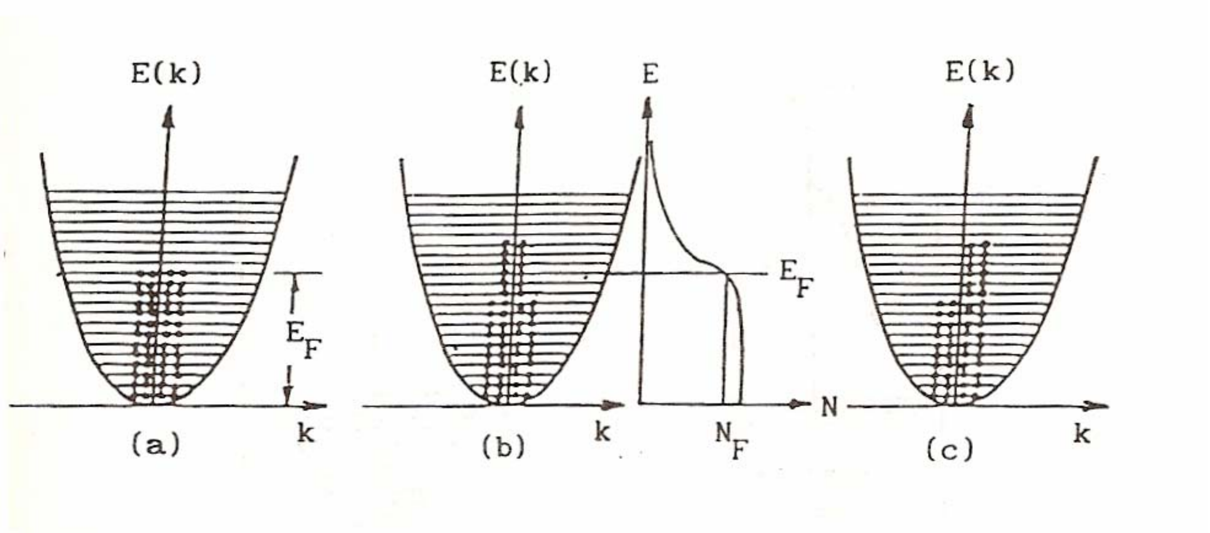

Fig. 4.6

According to the free electron model there does not exist forbidden bands for electrons. This statement does not cover the reality. Applying periodic potential we have a better approach of the real situation, since the positions of the atomic cores are periodic and also atomic core – electron interaction exists (Fig. 4.7).

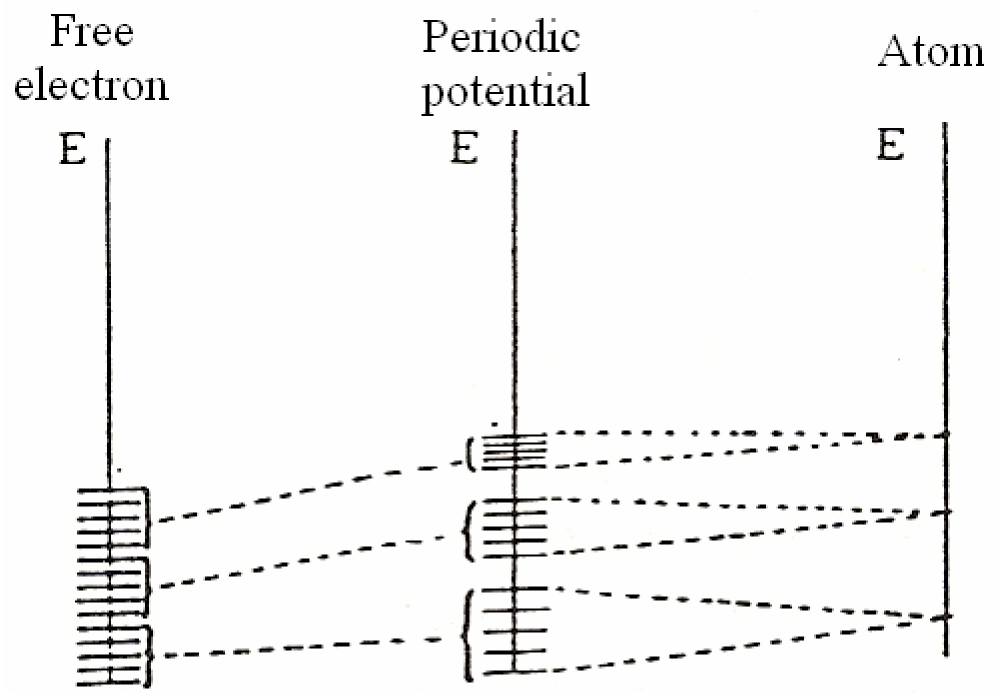

Fig. 4.7

The region $-\frac{1}{d} \leq k \leq +\frac{1}{d}$ region is the first Brillouin zone (d is the distance of the lattice points, Fig. 4.5). The behaviour of the potential in all other zones of $\frac{2}{d}$ width is similar, therefore the investigation of the 1st zone is sufficient. Assuming periodic energy function and solving the Schrödrnger equation of the problem the solution yields broader or thinner energy bands and between them broader ot thinner forbidden bands. Practically, one fobidden band exsist between two allowed bands. The lower band is the *valence band*, the upper one is the *conducting band.*

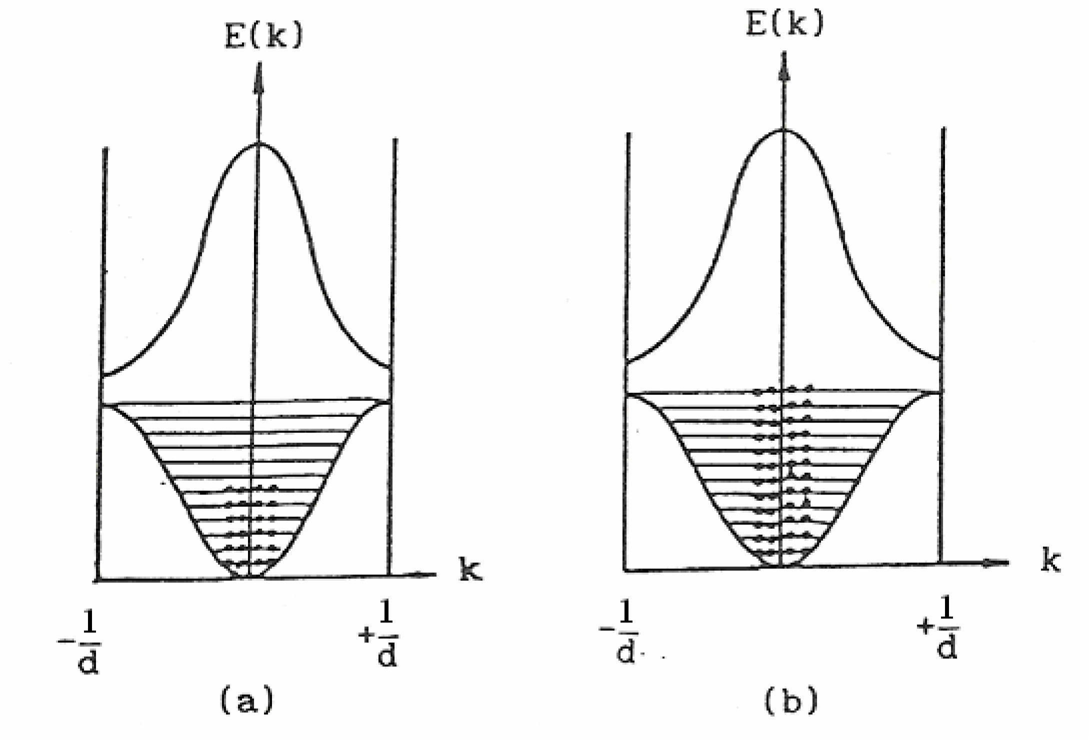

Fig. 4.8

Fig. 4.8 presents the conducting band (a) and the filled valence band (b) in the first Brillouin zone of a one-dimensional crystal lattice. The figure (a) contains empty levels over the filled ones, while in figure (b) all levels are filled. The levels of minimal energy are in both case at k=0, the levels of minimal energies of the upper bands are alway at $\pm\frac{1}{d}$. Further Brillouin zones are built with zone shifts of $\pm\frac{2}{d}$.

In real 3D crytals the valence and conducting bands can touch one another, this is a *conducting crystal*. If these two bands are very close, the charge transfer is easy, the crystal is a *semiconductor*. If the energy difference between the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) is not higher than $10 \times kT$, i.e. 0.26 eV (2.58 kJ/mol) the crystal is regarded as conductor. If the forbidden band is broader, the crystal is regarded as *insulator*.

In conductors the electrons conduct. In undoped or natural semiconductors the electrons conduct, or the electron gap (crystal defect). The gap is filled with electron jump from core to the other one, and a new gap will build. One can regard the movement of the gap as moving positive charge.

The semiconductors where the electrons conduct are *n-type semicondutors*, those with electron gap are *p-type semiconductors*. The undoped semiconductors have a limited conductivity, this the *intrinsic conductivity*.

Artificial semiconductors are manufactured with doping of atoms. The doped atoms are built in into the crytal lattices or are defect places. These atoms build an extra band between the valence and the conducting bands. In n-type doped semiconductors the doped atoms have electron excess (e.g. As $4s^2p^3$ is the electron donor in Si lattice $3sp^3$, Fig. 4.9a) and under external voltage these electrons move to the conducting band. In p-type doped conducting semiconductors the doped atom (like In $5s^2p^1$, electron aceptor in Si lattice, $3sp^3$, Fig. 4.9b) has electron gap. Under external electric voltage the electrons move from the very close new valence band to the acceptor level, building a conducting level. This seems in this case like the movement of a positive charge (p) in opposite direction of the electrons.

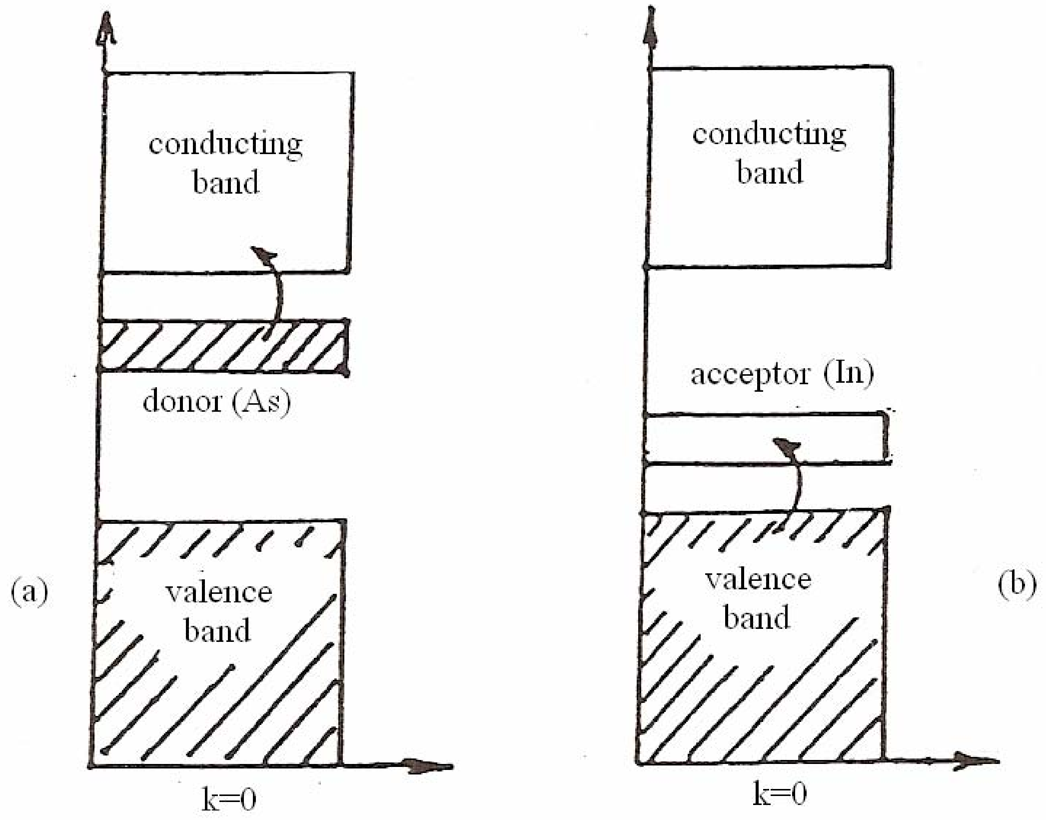

Fig. 4.9