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The Quantum Mechanics Aspect of Structural Transformations in Nanosystems

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1. Introduction

Theoretical and experimental investigations of size effects have made a substantial contribution to the development of nanophysics and nanochemistry. However, a great deal needs to be done in this field. Experimental results are not necessarily consistent with the traditional concepts. In particular, the melting temperature of small nanoparticles unexpectedly turned out to be higher than the melting temperature of a macroscopic sample of the same chemical composition [1].

It is this chemical composition of a macroscopic system that determines its melting temperature T_m , the specific heat of melting Q_m , and the entropy of melting S_m . These quantities do not depend on the number M of atoms (in the limit, $M \rightarrow \infty$). This statement ceases to be valid for relatively small systems. In the given case, it is necessary to take into account the dependences of the quantities T_m , Q_m , and S_m on the number M of atoms. Moreover, as the size of the system decreases, the interpretation of the physical quantities T_m , Q_m , and S_m should be refined. Indeed, one molecule, for example, the hydrogen molecule, cannot melt, because its dissociation occurs with an increase in the temperature. In this respect, it is advisable to analyze the structural transformations in nanosystems within a unified approach of the first principles of quantum mechanics and statistical physics.

2. Quasiclosed ensembles

In the framework of classical physics each structural modification is set by the vector

$$\mathbf{R} = (\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_i, \dots, \mathbf{r}_M), \quad (1)$$

where $\mathbf{r}_i$ are the radius vectors of all atomic nuclei of the polyatomic system. But the atomic nucleus is not a mathematical point whose position is unambiguously determined by the vector $\mathbf{r}_i$. The motion of microparticles is not characterized by the trajectory $\mathbf{r}_i(t)$. One can speak solely about the sites of their localization. In the case of condensed systems the size of the sites of atomic nucleus localization is much smaller than the interatomic distances and is a tenth-hundredth of an angstrom. Therefore, one of the ways to make a brief quantum-mechanical description of the structure $\mathbf{R}$ consists in setting the coordinates $\mathbf{r}_i$ (1) of the centers of these sites.

As a rule, numerous quantum states forming a quasiclosed ensemble correspond to each memorized macrostate (to each structural modification of $\mathbf{R}_k$). This raises the question about the number $G^{(0)}$ of different quasiclosed ensembles.

The magnitude of $G^{(0)}$ cannot be evaluated without application of quantum-mechanical methods. The point is that the components $\mathbf{r}_i$ of the vector $\mathbf{R}$ (1) can vary continuously, i.e. there exists a continuum of various structures (different vectors $\mathbf{R}_k$), which cannot even be numbered with the help of the index k , if it has solely integer values. This hampers the determination of the number $G^{(0)}$ of different structural modifications. In a quantum-mechanical description of a structure the superfluous detailing is useless altogether since according to quantum mechanics, a system is usually localized not at one point $\mathbf{R}_k$ but in a certain volume (cell Ω_k). The set of all cells Ω_k is countable. It is this circumstance that allows one to speak about the number $G^{(0)}$ of different structural modifications of the condensed system with a fixed chemical composition.

In order to find the numerical value of $G^{(0)}$ it is necessary to consider primarily the problem of distribution of quantum states over different quasiclosed ensembles. Some of these are formed by the microstates corresponding to one of the free energy minima. The latter holds only for stable and metastable systems. In the overwhelming majority of cases we are dealing however with nonequilibrium systems, the thermodynamic potentials of which are far from being extreme.

Thus structural modifications of the vitreous state are not characterized by the Gibbs energy minimum. Each of them is described by its intrinsic quasiclosed ensemble. Their macroscopic properties are invariable because a quite definite structural modification corresponds to each ensemble. It is for this reason that glasses are kinetically frozen nonequilibrium systems, the properties of which virtually do not change over the long time interval $t_{\max}$. The same may also be said about the overwhelming majority of noncrystalline substances, many of which are already widely used for recording information.

The class of various quasiclosed ensembles (different macrostates memorized by the system with a fixed chemical composition) is extraordinarily broad. Their number is substantially larger than the number of Gibbs energy minima.

All atomic configurations $\mathbf{R}_k$ (1) of an ideal monatomic gas are equiprobable. Condensed systems are characterized by the totally opposite situation. Therefore, it is not surprising that some of their structural modifications may be frozen (memorized) for a long time interval $t_{\max}$. Let us illustrate what has been said above in the framework of the adiabatic approximation.

3. Adiabatic approximation

The adiabatic approximation [2] is based on the considerable differences in the masses of electrons and nuclei, which makes it possible to describe their motions separately well. Being light particles, the electrons 'succeed' in adapting themselves to the instantaneous configuration $\mathbf{R}$ (1) of the atomic nuclei, the latter in turn 'notice' only the averaged disposition of electrons.

In the zero approximation the atomic nuclei are regarded to be at rest [$\mathbf{R} = \text{const}$ (1)]. In this case, the wave function $\Phi_j(\mathbf{R}, \mathbf{X})$ of the j -th stationary quantum state of the electron subsystem satisfies the equation [3]

$$\hat{H}\Phi_j(\mathbf{R}, \mathbf{X}) = U_M^{(j)}(\mathbf{R})\Phi_j(\mathbf{R}, \mathbf{X}), \quad (2)$$

where $\hat{H}$ is the Hamiltonian of electrons at fixed nuclei, which represents the sum of the total Coulomb energy of the interaction of atomic nuclei and electrons, the operator of the spin-orbital interaction of electrons and the operator of the kinetic energy of electrons; $\mathbf{X}$ is the sum of spatial and spin variables of all electrons of the system under consideration; $U_M^{(j)}(\mathbf{R})$ is the adiabatic electron term (Fig. 1), which in the case of a polyatomic system ($M > 3$) usually has a great number of different physically non-equivalent minima $\mathbf{R}_k$ [4]. The Hamiltonian H does not contain any operator of the kinetic energy of atomic nuclei and, consequently, is the operator of the energy of the system under consideration for the fixed atomic configuration $\mathbf{R}$.

When the motion of atomic nuclei does not induce any transitions between different electronic states, the function $U_M^{(j)}(\mathbf{R})$ (2) may be interpreted as the potential energy of the nuclei corresponding to the j -th electronic state. In this case their motion takes place in the potential field of $U_M^{(j)}(\mathbf{R})$.

Therefore, the nuclear wave function $\chi_j(\mathbf{R}, E)$ satisfies the Schrödinger equation [3]

$$(\hat{T} + U_M^{(j)}(\mathbf{R}))\chi_j(\mathbf{R}, E) = E\chi_j(\mathbf{R}, E), \quad (3)$$

in which in contrast to (2), there is no variable $\mathbf{X}$ corresponding to the electron subsystem. Here, T is the operator of the kinetic energy of atomic nuclei; E is the energy of the stationary quantum state. The chemical composition $\mathbf{n}$ determines unequivocally the explicit form of equations (2) and (3). The components of the vector $\mathbf{n}$ are the relative concentrations of atoms of each species which form the system under consideration.

Their different solutions describe various modifications of a substance with a fixed composition. This can serve as the basis for classification of these solutions. Thus in the case of selenium some solutions may be attributed to the fluid state, others - to definite crystalline modifications, to amorphous modifications, to the vitreous state, to films, etc. However, it is most advisable to base the discussed classification of solutions of equations (2) and (3) on the structure $\mathbf{R}$ (1)

because the information about individual peculiarities of a polyatomic system is eventually stored in the mutual disposition of its atomic nuclei. Any structural modification (e.g., the k -th modification) which is preserved at least over the time interval $t_{\max}$ is described by the wave functions $\Phi_j(\mathbf{R}, \mathbf{X})$ (2) and $\chi_j(\mathbf{R}, E)$ (3) localized near the point $\mathbf{R}_k$. (Fig. 1). The diversity of the latter actually determines all the states belonging to the k -th quasiclosed ensemble.

Usually one or a series of potential $\mathbf{R}_k$ minima correspond to the points $U_M^{(j)}(\mathbf{R})$, near which the motion of one or other structural modification takes place. In order to estimate the number of such points (the number $G^{(0)}$ of different quasiclosed ensembles), it is, as a rule, sufficient to consider only the minima of the adiabatic electron term $U_M^{(0)}(\mathbf{R})$ corresponding to the ground ($j = 0$) state of the electron subsystem¹.

The point is that the lifetimes τ_e of most excited states of the electron subsystem are relatively short ($\tau_e \ll t_{\max}$). Therefore, these states alone cannot form a quasiclosed ensemble, in the framework of which the k -th structural modification can be described over a long time interval $t_{\max}$. Its preservation is favored by the potential barriers surrounding the minimum $\mathbf{R}_k$ of the adiabatic electron term $U_M^{(0)}(\mathbf{R})$ (Fig. 1). If they are sufficiently high, then even the low-energy quasi-steady [5] states localized in the potential well $\mathbf{R}_k$ under consideration have larger [compared to $t_{\max}$] lifetimes τ_l which satisfy the inequalities

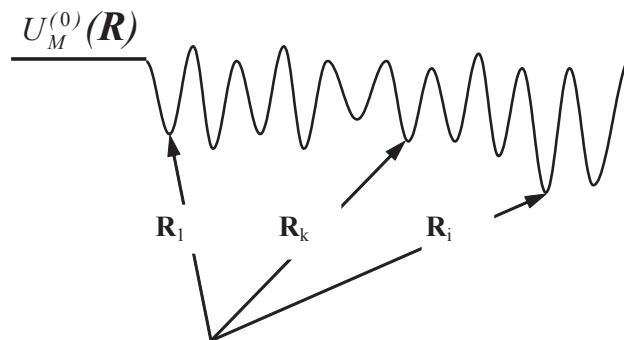


Figure 1. Adiabatic electron term $U_M^{(0)}(\mathbf{R})$. This figure is rather conditional because for polyatomic systems ($M > 3$) the function $U_M^{(0)}(\mathbf{R})$ is set, in conformity with (1), in the multidimensional space.

$$\tau_r \ll t_{\max} \ll t_l \quad (4)$$

where τ_r is the relaxation time of the phonon subsystem, which is usually appreciably shorter than the time $t_{\max}$ required for the preservation of structural modifications.

¹ Each minimum of the function $U_M^{(0)}(\mathbf{R})$ sets one of the equilibrium configurations $\mathbf{R}_k$. Crystalline nanoparticles correspond to the deepest minima (potential wells). Most minima correspond to different noncrystalline structures. Transition from one potential well to another ($\mathbf{R}_i \rightarrow \mathbf{R}_k$) means in the general case the rearrangement of all of the M atomic nuclei of the system. The adiabatic electron term $U_M^{(0)}(\mathbf{R})$ does not depend either on temperature or on the thermal prehistory, etc. According to (2), it is unequivocally determined only by the chemical composition. Various scenarios of the system behavior consist in the sequence of passage over potential wells [the minima of the function $U_M^{(0)}(\mathbf{R})$].

Consequently, quasiclosed ensembles may be formed by the stationary and quasi-steady [5] states with large lifetimes τ_1 (4). Usually these are low-energy states, which describe vibrational motion of atomic nuclei near one of the minima of the adiabatic electron term $U_M^{(0)}(\mathbf{R})$. Transitions between these states are not accompanied by any substantial changes in the $\mathbf{R}_k$ structure [6]. The k -th structural modification is preserved when only such transitions take place.

Thus, in order to preserve a polyatomic system, an exact copy and also the recorded information, it is sufficient that all changes occurring in the system do not extend outside the limits of one and the same quasiclosed ensemble. It is this ensemble that characterizes the properties of the system displayed during informational interaction [7].

The magnitude of $G^{(0)}$ can be estimated proceeding from the number $J(\mathbf{n}, M)$ of different minima of the potential $U_M^{(0)}(\mathbf{R})$. This approach allows a relatively simple derivation of numerical estimates as the function $J(\mathbf{n}, M)$ depends on only two arguments and, in addition, its determination is actually based on equation (2) when $j=0$. This unambiguous mathematical definition is useful not only for the problem of information copying and recording but also for considering a wide range of other issues [4].

4. Estimation of the number $G^{(0)}$ of different quasiclosed ensembles

For the number $J(\mathbf{n}, M)$ of different physically non-equivalent local minima of the adiabatic electron term $U_M^{(0)}(\mathbf{R})$, which corresponds to the ground electronic state of the electroneutral system consisting of M atoms, the following asymptotic formula [4] is valid as $M \rightarrow \infty$

$$\frac{1}{M} \ln J(\mathbf{n}, M) \sim \alpha_{\mathbf{n}}, \quad (5)$$

where $\alpha_{\mathbf{n}}$ is the positive parameter dependent solely on the chemical composition $\mathbf{n}$. The components n_i of the vector $\mathbf{n}$ are the relative concentrations of atoms of each type.

It follows from (5) that

$$J(\mathbf{n}, M) = \exp(\alpha_{\mathbf{n}} M + o(M)), \quad (6)$$

the function $o(M)$ satisfying the condition $\lim_{M \rightarrow \infty} o(M)/M = 0$. In other words, the number $J(\mathbf{n}, M)$ of different physically nonequivalent minima of the $U_M^{(0)}(\mathbf{R})$ potential exhibits a rapid exponential growth with the increasing number M of atoms forming the system with a fixed ($\mathbf{n} = \text{const}$) chemical composition. The numerical values of $\alpha_{\mathbf{n}}$ in relationship (6) usually differ from $\ln 2 \approx 0.69$ by smaller than one order of magnitude.

This fact is not surprising because the magnitude $J(\mathbf{n}, M)$ (6) takes into account all potentially possible structural modifications $\mathbf{R}_k$ (1) of a polyatomic system. These are structures of nanoparticles, liquid, glass, perfect crystal, crystals with different concentrations of particular defects, polycrystals, amorphous substances, amorphous and vitreous films, glass-ceramics and many others, including the structures of microheterogeneous materials storing the recorded information. These structures differ from each other not only in the location of particular defects, holes, etc. There exist other differences. For example, there are six equilibrium positions for each oxygen atom in the structure of β cristobalite (Fig. 2, positions 1–6) [6].

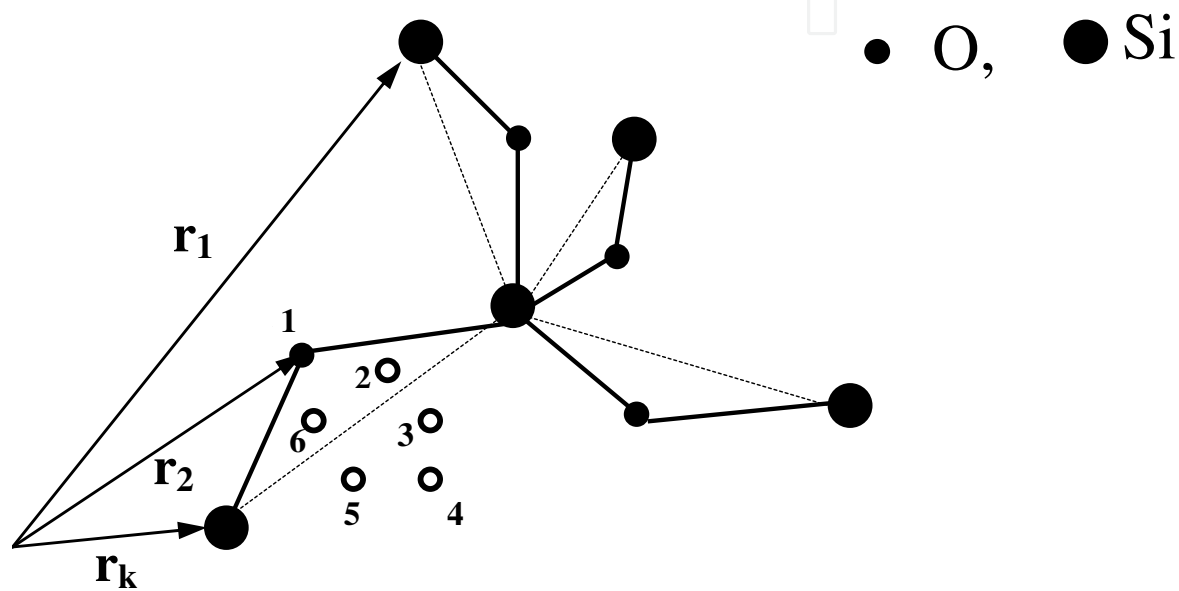


Figure 2. Structural fragment of β cristobalite (r_i are the radius vectors of equilibrium atomic positions).

The transitions between them are not accompanied by the formation (disappearance) of defects, holes, dangling chemical bonds, etc. Each structure thus formed is not an exact copy of other structures [7]. These configurations are also taken into account by relationship (6).

The diversity of elementary configurational excitations particularly involves small structural transformations. As a result of these transformations, the transition from one minimum of the adiabatic electronic term $U_M^{(0)}(\mathbf{R})$ to another minimum occurs through a correlated rearrangement of many atoms involved in a particular nanofragment. In this case, the distances between any pair of neighboring atoms change insignificantly as compared to the interatomic distances (Fig. 3) and, as a consequence, the short-range order is retained.

Specifically, small structural transformations occur in the glass transition range [4] (upon softening of a glass and melting of a crystal) when the coordination numbers remain virtually unchanged. Uncorrelated small structural transformations that proceed in different nanofragments of the melt upon its rapid cooling lead to generation of internal stresses in the resulting glass.

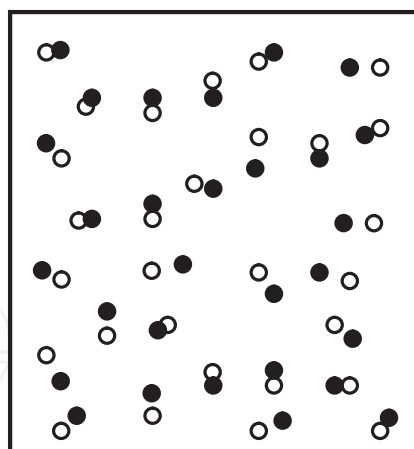


Figure 3. Schematic diagram illustrating a small structural transformation: ○initial and ●final positions of sites of atomic nuclei in a nanofragment.

The diversity of minima of the function $U_M^{(0)}(\mathbf{R})$ makes it possible to explain the possibility to vary properties of a material of the same chemical composition through preparation of its various modifications described by different quasiclosed ensembles.

Number $G^{(0)}$ of different quasiclosed ensembles satisfies the following relations :

$$\ln G^{(0)}(t_{max}, n, M) \leq \ln J(n, M) = (\alpha_n M + o(M)) \leq (B \times M + o(M)), \quad (7)$$

where constant B is determined by the identity

$$B \equiv \sup_n \alpha_n \quad (8)$$

It would not be particularly difficult to find the exact value of constant B (8) if the solutions of equation (2) at $j=0$ were known for the systems of various chemical compositions. Since this is not the case, one has to use model approaches. In their frameworks it is possible to calculate numerical values of the parameter α_n (5), (8) for specific systems. The results of such computations [4] support the following estimate:

$$B \approx 3 \quad (9)$$

It is difficult to investigate thoroughly all configurations of the polyatomic system, because their number is exponentially large [see relationship (6)]. In this respect, it is necessary to use model approaches. A model based on the Gaussian distribution is convenient for constructing the statistical thermodynamics of melting and softening of nanoparticles.

5. Model spectrum for the description of configurational excitations

In order to describe any equilibrium process, including the melting, in the framework of statistical thermodynamics [8], it is sufficient to know the time dependence of the statistical sum Z , which is uniquely determined by the temperature T , the energies E_j of stationary quantum states, and the multiplicity g_j of their degeneracy; that is

$$Z = \sum_j g_j \exp(-E_j / kT). \quad (10)$$

Here, k is the Boltzmann constant and $E_j < E_{j+1}$. This holds true for any system with a fixed number of particles from one elementary particle to inhomogeneous (specifically, multiphase) media.

The energy spectrum $\{E_j, g_j\}$ depends on the number M of atoms. Since the energy spectrum of a macroscopic system ($M \geq 10^{20}$) differs from that of a nanoparticle ($10^8 \geq M \geq 10$), the processes accompanying the melting of a macroscopic sample and a nanoparticle of the same chemical composition cannot not be completely identical. However, the specific features of these processes have much in common: in both cases, upon melting, the structure undergoes transformations, the system becomes microscopically labile, and the entropy and the internal energy increase abruptly.

In expression (10), the summation is performed over all possible configurations corresponding to relationship (6) and different vibrational states. By using the known analytical expression for the statistical sum of an oscillator [8], the sum of all terms associated with the i -th configuration $\mathbf{R}_i$ can be represented in the form $\tilde{g}_i \exp(E_i/kT)$.

This enables us to change over to the model partition function with due regard only for the configurations in which each configuration is included $\tilde{g}_i/\tilde{g}_1$ times, where $\tilde{g}_1$ corresponds to the configuration with a minimum energy². The ratios $\tilde{g}_i/\tilde{g}_1$ actually take into account the role of the phonon subsystem in the melting.

The energies $E_i = U_M^{(0)}(\mathbf{R}_i)$ of the equilibrium configurations (2) of the polyatomic system are conveniently calculated per atom; that is,

$$\varepsilon_i = E_i / M \quad (11)$$

The spectrum of numerical values of the energies ε_i (fig.4) depends on the number of atoms M . The level with the minimum energy $E_1 = 0$ is assumed to be nondegenerate: $g_1 = 1$. The distribution of levels located in the energy range between $M\varepsilon_g$ and $M\varepsilon_c$ is approximated by the Gaussian distribution

² In this case, the number of configurations can be determined from formula (6), in which the numerical value of the parameter α_n changes insignificantly.

$$N(E) \sim \frac{\sigma(E-E_0)}{\gamma\sqrt{2\pi M}} \exp\left\{M\alpha_n - 0.5\left(\frac{E-Mh}{\gamma\sqrt{M}}\right)^2\right\} \quad (12)$$

Here, E_0 is the minimum energy necessary for transforming the system from the ground state into the excited state, $\sigma(E-E_0)$ is the step function,

$$\gamma = 0.5(\varepsilon_c - \varepsilon_g) / (2\alpha_n)^{1/2} \quad (13)$$

$$h = 0.5(\varepsilon_g + \varepsilon_c). \quad (14)$$

From the distribution density $N(E)$ (12), we derive the following analytical expression for the statistical sum (10) (statistical integral)

$$Z = 1 + \left\{ \exp M\left(\alpha_n - \frac{h}{kT} + \frac{0.5\gamma^2}{(kT)^2}\right) \right\} \Phi\left(\frac{Mh-E_0}{\gamma\sqrt{M}} - \frac{\gamma\sqrt{M}}{kT}\right) \Bigg| \Phi\left(\frac{Mh-E_0}{\gamma\sqrt{M}}\right), \quad (15)$$

where $\Phi(x) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^x \exp(-0.5x^2) dx$ is the normal distribution function. The analytical expression (15) permits us to analyze not only the dependence of the statistical sum on the number M of atoms. The corresponding dependences can be obtained for all quantities that are uniquely defined by the statistical sum Z . In particular, these are the melting temperature, the heat of melting, and the entropy of melting.

In the limit $M \rightarrow \infty$, the melting temperature T_m is given by the expression [4]

$$T_m = (\sqrt{\varepsilon_g} + \sqrt{\varepsilon_c})^2 / 4k\alpha_n \quad (16)$$

In the same limit, the stepwise increments of the energy $\Delta\varepsilon$ (fig.4) and the entropy Δs upon melting per atom are represented by the formulas

$$\Delta\varepsilon = (\varepsilon_g \varepsilon_c)^{1/2}, \quad (17)$$

$$\Delta s = 4k\alpha_n (\varepsilon_g \varepsilon_c)^{1/2} (\sqrt{\varepsilon_g} + \sqrt{\varepsilon_c})^{-2} \leq k\alpha_n. \quad (18)$$

It should be noted that, at the melting temperature T_m , the following inequalities are satisfied:

$$\varepsilon_c / k\alpha_n \geq T_m \geq \max\{ (\varepsilon_g \varepsilon_c)^{1/2} / k\alpha_n, \varepsilon_c / 4k\alpha_n \}. \quad (19)$$

Before melting, the energy is minimum. Without loss of generality, this energy can be taken equal to zero. In the course of melting, there occurs a stepwise transition within the energy band $[\varepsilon_g, \varepsilon_c]$, which involves energies of the majority of the equilibrium configurations (fig.4). The width $(\varepsilon_c - \varepsilon_g)$ of this band is proportional to the root-mean-square deviation of the numerical values of the energies ε of different configurations.

Upon melting, the structure undergoes transformations. Furthermore, the nanoparticle becomes labile. In particular, the nanoparticle changes in shape, because, after melting, there occur spontaneous transitions between the structural modifications with close energies in the energy band $[\varepsilon_g, \varepsilon_c]$ (fig.4).

The notion of the “melting of nanoclusters” has already been used [1]. It is obvious that the processes accompanying the melting of a macroscopic sample and a nanoparticle cannot not be completely identical. However, the specific features of these processes have much in common. In both cases, upon melting, the structure undergoes transformations, the system becomes labile, and the entropy and the internal energy increase abruptly.

According to relationships (16-18), the melting temperature T_m can be described by one more expression

$$T_m = \Delta\varepsilon / \Delta s, \quad (20)$$

which coincides with the known expression that relates the heat $\Delta\varepsilon$, the entropy Δs , and the temperature T_m of the transition [9]. Note that, in the case of the macroscopic system, the heat of melting $\Delta\varepsilon$ and the entropy of melting Δs per atom in relationship (20) are independent of the number M of atoms forming the macroscopic system, whereas the opposite situation is observed for the nanoparticle. The spectrum of energies ε of equilibrium configurations can even radically change (fig.4).

For example, the two-atom system ($M = 2$) has only one equilibrium configuration $J(\mathbf{n}, 2) = 1$ and the energy band $[\varepsilon_g, \varepsilon_c]$ is absent. Since the structure should change upon melting (there should occur a transition from one equilibrium configuration to another equilibrium configuration), the melting of two-atom systems, in principle, is impossible.

However, the above concept is inapplicable to relatively small nanoclusters consisting of 13 atoms with $J(\mathbf{n}, 13) = 1478$ different configurations (different energy levels) [10]. In this case, the energy spectrum can be described by the Gaussian distribution but with parameters different from those used for the macroscopic system.

Relationships (16)–(20) are also valid in the mesoregion where the number of atoms M is larger than two but is not sufficient for the applicability of the asymptotic relationship (5), which allows one to estimate the number of equilibrium configurations of the macroscopic system.

For nanoclusters, relationships (16) and (18) should contain the parameter $\tilde{\alpha} = \{\ln(J(n, M) - 1)\} / M$ instead of the parameter α_n involved in relationship (5). In the case of a two-atom system, we have the parameter $\tilde{\alpha} = \{\ln(J(n, 2) - 1)\} / 2 = -\infty$. For a nanocluster consisting of 13 atoms, we should use the parameter $\tilde{\alpha} = \{\ln(J(n, 13) - 1)\} / 13 \approx 0,56$. The change in sign of the parameter $\tilde{\alpha}$ indicates that, for a relatively small number of atoms M , which satisfies the inequality $M > 2$, the parameter $\tilde{\alpha}$ can turn out to be close to zero.

Therefore, the numerical value of the parameter in the mesoregion can appear to be considerably smaller than the parameter α_n involved in relationship (5) and used for calculating the melting temperature of the macroscopic sample according to relationship (16). This circumstance is responsible for the observed increase in the melting temperature of sufficiently small nanoparticles as compared to the macroscopic sample.

Since the parameter $\alpha_n(\tilde{\alpha})$ is equal to the natural logarithm of the number of energy levels (equilibrium configurations) in the energy band $[\varepsilon_g, \varepsilon_c]$ (fig.4), the product $k\alpha_n$ in relationship (18) gives an estimate from above for the jump Δs in the configurational entropy upon melting. In the case where $\alpha_n(\tilde{\alpha}) \rightarrow 0$, we have $\Delta s \rightarrow 0$. In other words, the decrease in the parameter $\alpha_n(\tilde{\alpha})$, according to relationship (18), leads to a decrease in the entropy of melting Δs and, consequently, to an increase in the melting temperature T_m in accordance with relationship (20).

Therefore, generally speaking, the melting temperature of macroscopic samples can be lower than the melting temperature of nanoclusters of the same chemical composition. Moreover, there are other specific features of melting of nanoparticles. Particularly, this refers to the melting temperature range ΔT_m , which, unlike the corresponding range for macroscopic systems, is not a small quantity.

6. On the temperature ranges of melting and softening

A decrease in the number of atoms M results in an increase in the temperature range ΔT_m of the phase transition [10]; that is,

$$\Delta T_m \approx T_m (2n \ln 10) / (M \tilde{\alpha}). \quad (21)$$

Here, n is a natural number which, at the boundaries of this range, determines a low probability $p = 10^{-n}$ that the system is in the liquid state before melting and in the solid state after melting, respectively.

At $n = 3$ and $\tilde{\alpha} = \ln 2$, expression (21) can be represented in the form

$$\frac{\Delta T_m}{T_m} M \approx 20. \quad (22)$$

As follows from formula (22), the quantities ΔT_m and T_m for nanoparticles containing of the order of ten atoms are comparable in magnitude. By contrast, the temperature range ΔT_m for macroscopic systems ($M \sim 10^{23}$) is nearly equal to zero.

According to relationship (22), the temperature range ΔT_m is relatively small

$$\frac{\Delta T_m}{T_m} \ll 10^{-2}. \quad (23)$$

only for systems involving a considerable number of atoms

$$M \gg 2000. \quad (24)$$

Otherwise, the quantity ΔT_m should not be ignored. Therefore, specific analogy can be drawn between the melting of nanoparticles and the softening of glasses.

Actually, the microscopic mechanism of glass softening is associated with the independent structural excitations in medium-range order nanofragments. Their initial structures, as a rule, are not exact copies of each other [7]. As a consequence, since the glass softening is a thermodynamically nonequilibrium irreversible process, it occurs in a specific temperature range ΔT_g rather than at a fixed temperature T_g .

Therefore, the glass softening and the transition of the nanoparticle to the microscopically labile state proceed in a particular temperature range rather than at a fixed temperature. Both these phenomena are responsible for the inelastic compliance of the system. This manifests itself as a viscous flow for macroscopic systems and a possibility of changing the shape due to the spontaneous transitions between different structural modifications with close energies within the band $[M\varepsilon_g, M\varepsilon_c]$ (Fig. 4) for nanoparticles.

The transition of the nanoparticle to the microscopically decrease in the temperature, the nanoparticle structure does not always revert to the initial state and, as in the case of the glass transition, one of the intermediate structures can turn out to be frozen. The question arises of whether the transition of the nanoparticle to the microscopically labile state in similar situations can be always interpreted as softening.

7. Admissible states

The freezing is a thermodynamically nonequilibrium process. The concept of “admissible states” [8] is useful when constructing the statistical thermodynamics of these processes. Not all states can occur for the observation time of a specific system. The states in which SiO_2 has a crystalline form are inadmissible at low temperatures if the object was initially in the vitreous form: this compound in experiments at low temperatures does not transform into quartz

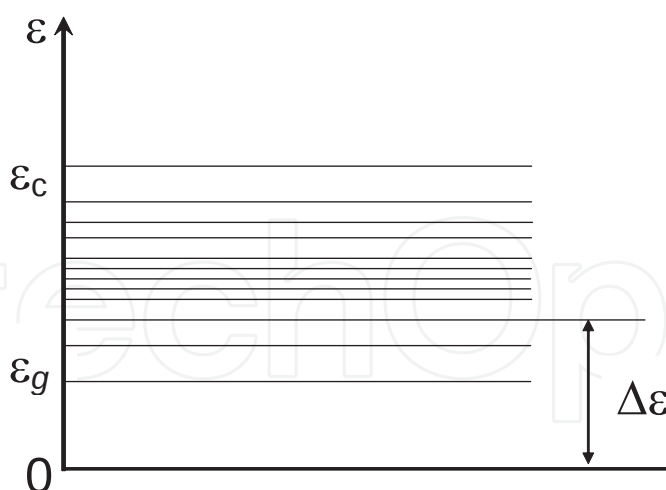


Figure 4. Spectrum of energies ε per atom for equilibrium configurations of the polyatomic system.

during our life. We assume that all quantum states are admissible if they are not excluded according to the definition of the system or the chosen time scale [8].

Generally speaking, the spectrum of admissible states changes depending on the prehistory of the formation of the polyatomic system. The same holds true for numerical values of the parameters γ , h , α_n , ε_c , and ε_g (12)–(14) used for approximating the spectrum of admissible states. Let us assume that the initial state of the nanoparticle is in the band $[M\varepsilon_g, M\varepsilon_c]$ (Fig. 4) and the state with the minimum energy $\varepsilon = 0$ is inadmissible³. Then, the spectrum of admissible states is approximated only by distribution (12). In this case, we have $\varepsilon_g = 0$ and the heat of melting $\Delta\varepsilon$ according to relationship (17) is equal to zero. As a consequence, we cannot speak about the melting, even though the thermodynamically nonequilibrium transition to the microscopically labile state is possible upon heating. This transition occurs in the temperature range ΔT_g at the softening temperature T_g , which can be estimated as follows [4]:

$$T_g \sim \gamma / (k(2\alpha_n)^{1/2}) \quad (25)$$

The softening temperature T_g and the boundaries of the softening range ΔT_g are kinetic parameters and depend on the prehistory of the compound. By contrast, the melting is a thermodynamically equilibrium process, which proceeds at a fixed temperature. As a result of melting, the structure of the macroscopic system is radically changed from crystalline to disordered. Upon softening, the short-range order in the atomic arrangement is retained. Consequently, the structure undergoes an insignificant transformation. Correspondingly, a change in the internal energy is also small and, therefore, the notion of “the heat of softening” does not exist.

³ The lower level corresponds to the crystal. This level is excluded when constructing the statistical thermodynamics of glasses and glass-forming melts. This level is not used for describing the softening and glass transition.

In the case of macroscopic systems, the above criteria allow us to distinguish rather simply the melting from softening. By contrast, not all transitions of the nanoparticle from the solid state to the microscopically labile state can be uniquely interpreted as melting or softening, because there are intermediate situations.

Specifically, these situations involve a thermodynamically equilibrium transition that results in an insignificant change in the structure (the short-range order is retained). In this case, the jump $\Delta\varepsilon$ (17) in the internal energy

$$\Delta\varepsilon \ll 10^{-2} \text{ eV} \quad (26)$$

is small as compared to the heat of melting of the macroscopic system of the same chemical composition per atom. It is unlikely that this transition should be treated as melting. However, since the transition under consideration is thermodynamically equilibrium, it is not advisable to identify this transition with the softening.

Eventually, it is important to know the spectrum of admissible states and the parameters γ , h , α_n , ε_c and ε_g (12)–(14). This makes it possible to reveal the energy characteristics of elementary structural excitations of the nanoparticle. In particular, the transitions between the equilibrium configurations closest in energy in the band $[M\varepsilon_g, M\varepsilon_c]$ (Fig. 4) are accompanied by the absorption (emission) of longwavelength photons [4]. Their frequencies can be estimated from the relationship

$$\nu[\text{Hz}] \sim 2 \cdot 10^{14} M (\varepsilon_c - \varepsilon_g) \exp(-\alpha_n M). \quad (27)$$

According to relationship (27), at $M = 100$, $\alpha_n = 0.1$, and $(\varepsilon_c - \varepsilon_g) = 0.1 \text{ eV}$, we obtain a frequency $\sim 10^{11} \text{ Hz}$, which corresponds to the microwave range of electromagnetic radiation.

It follows from relationship (27) that the elementary structural excitations of nanoparticles can be attended by emission (absorption) of photons with frequencies in the microwave, radio-frequency, and low-frequency ranges. It was experimentally demonstrated that the microwave radiation can accelerate chemical reactions by a factor of several tens and even several hundreds [11]. The microscopic mechanism of this phenomenon is not clearly understood. However, it is unquestionable that this mechanism is not reduced only to heating.

8. Conclusions

A detailed (on the microscopic level) analysis of the processes that occur upon transition of nanoparticles to the microscopically labile state stimulates consideration of a number of fundamental problems. Their solution provides a deeper insight into the specific features of the nanoworld. Indeed, the melting and softening cannot proceed in the absence of an exponentially large number of various structural modifications (6). However, up to now, most

attention has been focused on relatively stable structures. The number of these structures for a nanocluster composed of 13 atoms is considerably smaller than 1478 [10].

The other structural modifications have not been adequately investigated, even though their role is important not only for the transition of the nanoparticle to the microscopically labile state. Many chemical transformations represent a sequence of transitions between unstable modifications. They should be taken into account when developing methods for synthesizing nanostructured functional materials with controlled properties.

The majority of nanoparticles of the same chemical composition exhibit similar additive properties. It is sufficient to investigate one of these nanoparticles in order to judge the properties of the other nanoparticles. However, there are “special” nanoparticles. Their properties differ noticeably from the statistical-mean properties and can be unique as compared to those of macromolecules and compact materials. Owing to this uniqueness, it is these nanoparticles that are of most interest for the nanotechnology.

Certainly, special nanoparticles are small in number. Among an exponentially large number (6) of various nanoparticles of the same chemical composition, the choice of a special nanoparticle with required properties is not a simple problem. Moreover, it is not a priori known whether there exists this nanoparticle in principle.

Furthermore, the potential possibility of occurring a large number of similar structural modifications different from the required modification complicates the reproduction of an exact copy [7] of the nanoparticle under consideration. That is why the reproducibility is one of the key problems of the nanotechnology.

In actual practice, the special nanoparticle cannot be synthesized in an accidental way. The traditional methods are not necessarily effective because the vast majority of the currently used chemical reactions belong to “disorganized” reactions in which particles (molecules, ions, atoms, radicals) react as a result of random collisions.

In order to solve many problems of nanotechnologies, it is required to control chemical processes on the microscopic level. It is necessary to design nontraditional methods based on nonequilibrium processes [12].

In particular, it seems likely that the use of electromagnetic radiation holds considerable promise. The methods of microwave chemistry have already been used to produce nanopowders [11].

The problem associated with the synthesis of special nanoparticles would be completely solved if the technique for preparing any controlled equilibrium configuration $\mathbf{R}_i$ of atomic nuclei (Fig. 1) would be developed. In general, for this purpose, it is necessary to know how to operate not with one atom but with many atoms according to a special program [13], which represents algorithmic information. It should be noted that the information aspect of microscopic processes [14] has come under the scrutiny of science only in recent years.

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