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Amorphous state in the substance hierarchy classification

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Abstract. It is justified that the amorphous state are such substances, which are realized in the solid area of the phase diagram. At the same time ordered or disordered by a particular physical parameter can be any aggregate state of matter. Therefore, solid state combines two large classes of substances: ordered solids (mostly crystals) and disordered solids (or amorphous). It is shown that the main parameters of this separation are the geometric characteristics of the spatial arrangement of the particles of matter among themselves, which defines a topological order of the solid. Thus, the terms "disordered" can be applied to any state of matter, and the term "amorphous " - only for solid systems.

Keywords: aggregate states, phase, amorphous materials

Intensive studies in the field of amorphous materials are being carried out now in growing scale. The interest in these studies is due, on the one hand, to a number of unique properties that favor their wide practical application. On the other hand, the studies of the disordered systems are a hot topic in view of the fundamental science. The problem of description of the physical properties of the disordered systems is still one of the most intriguing and not completely solved problems of the modern condensed state physics. The principal question of the above studies is correlation of the physical and chemical properties of the amorphous substances with their atomic structure. About ten different models and axiomatic approaches are available here, and this could not be justified taking into account the up-to-date successes in the amorphous state science.

It follows from the mentioned above that, when considering the general questions of the amorphous state of the substance, it is important to establish the hierarchy of different terms according to the attribute 'general – partial' and assign them a clear physical sense. Consider first the hierarchy of the terms used by the most of researchers dealing with the condensed state of the substance.

In accordance with the generally accepted classification, a certain substance in the fixed external conditions may have one of four aggregate states: solid, liquid, gaseous and plasma states. Each of the above states has its own region in the generalized phase diagram (fig. 1). The field of the solids having polymorph modifications can be divided into several subregions and each of them corresponds to a certain equilibrium or metastable phase of the substance (the α-, β- and γ-phases in fig. 1).

The principal criterion of the above division is the ratio e of the average kinetic energy of the structural particles to the potential energy of their interaction. Parameter e and, respectively, the realized aggregate state are determined by the physical conditions of the substance, mainly by the temperature T and the pressure p. Therefore, in the first approximation $e = e(p,T)$. For solids $e(p,T) \ll 1$ (in the ideal case $e(p,T) \to 0$), for liquids $e(p,T) \approx 1$, for gases and plasma $e(p,T) \gg 1$ (in the ideal case $e(p,T) \to \infty$). The motion of atoms and molecules in different aggregate states also differs significantly.

In particular, the structural particles of the substance in the gaseous state are not bound or are very weakly bound by mutual interaction forces and move slowly filling the whole volume. At the transition of gases into liquid the translation movement of the structural particles extremely slows down, while the interparticle attractive forces increase resulting in the formation of quite strongly bound groups of atoms, i.e. short range order (SRO). The value $e(p,T) \approx 1$ for liquids means that the ordering potential energy of interaction of the structural particles and the disordering kinetic energy of the thermal motion of the structural particles have comparable values. Therefore, the motion of the structural particles in the liquid combines their continuous oscillations around the equilibrium positions and frequent leaps from one equilibrium position to another one. Each 'leap' occurs when the structural particle receives the activation energy sufficient for breaking its bounds with adjacent structural particles with the transition to the neighborhood of other structural particles. The typical leap frequencies for the low-molecular liquids reach 10^{11}–10^{12} s^{-1}. Such specific character of the structural particles interaction and motion stipulate fluidity and almost continuous structural change of liquid with temperature of the system.
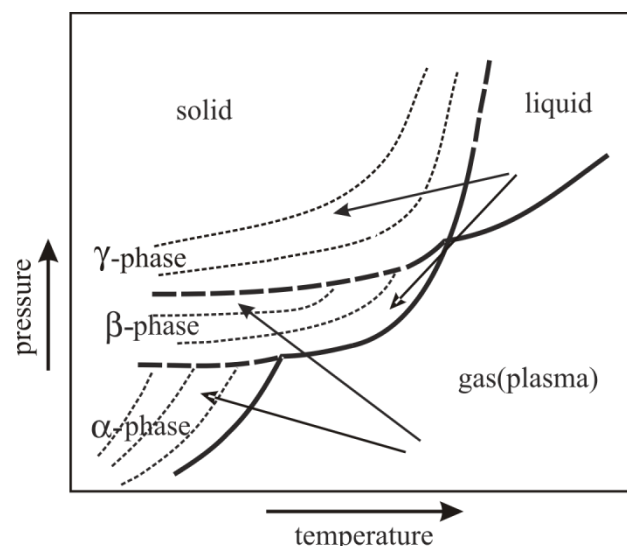

Fig. 1. Simplified phase diagram for a certain substance in the pressure-temperature coordinates (arrows indicate two basic types of transitions between the aggregate states used to produce amorphous materials)

In the solid, $e(p,T) \ll 1$ and, therefore, the motion of the structural particles occurs only in a form of the continuous oscillations around the equilibrium position. The leaps from one equilibrium position to another one occur

so rarely that in the ideal case could be neglected. As a result it is assumed that the atomic structure in solids is fixed and does not vary with temperature within the limits of occurrence of this phase.

Liquids and solids are much closer to each other according to their properties. This enables them to be combined into the same group of substances – the condensed media. The availability of a certain order in the locations of the structural particles with respect to each other due to quite close positioning and stronger interaction with each other is a distinctive feature of the condensed state of the substance. Dependent of the character of this order the liquid or solid could be classified as ordered or unordered condensed state.

The transition between the aggregate states is accompanied by a leap-like or continuous change of parameter $e(p,T)$ that reflects the character and dynamics of the change of intermolecular (interatomic, interionic) distances and corresponding interactions. At the same time, the other properties of the substance – free energy, entropy, density etc – are changed at the transition point. The following are the examples of the continuous processes: vitrification, glass transitions to the melted state with increasing pressure and temperature, liquid transitions to the gaseous state above the critical state.

The possibility of the continuous transitions and occurrence of the substances simultaneously possessing specific properties of different aggregate states (amorphous solids, liquid crystals, highly-elastic polymers etc) at first sight indicate some conventionality of differentiation of the substances according to their aggregate states. However, if one takes as a basis only the criterion $e(p,T)$ and the relevant character of motion of the structural particles, then any substance in the specific fixed conditions could be unambiguously related to the particular aggregate state.

In the modern condensed-state physics, the notion of the phase is being used more widely and is stricter than the notion of the aggregate state. At the same time, the notion of the aggregate state is wider than the notion of the phase, because for many materials there exist several stable and metastable phases both in the solid and in the liquid aggregate states. While at the transition from one aggregate state to another the parameter $e(p,T)$ changes significantly, the phase transition is accompanied by the transition from one aggregate state to another. If the parameter $e(p,T)$ does not change considerably, then the phase transition takes place within the limits of the same aggregate state, where several phases do exist.

It is often assumed from the standpoint of the thermodynamical phase with the account made for metastability that the amorphous substance is a super-cooled liquid. However, by definition, the phase is the equilibrium (or metastable) homogeneous state of the substance and the transitions between the phases are accompanied by the change of the physical properties. This means that consideration of the amorphous substances as the super-cooled liquids is related to the presence of the word 'metastable' in the definition of the thermodynamical phase. However, the solid state may also be metastable. Moreover, metastability (non-equilibrium) is more typical for the solid state than for the liquid, thus, from the viewpoint of definition of the thermodynamical phase, there are no serious grounds for the transition from the solid body to the super-cooled liquid when defining the amorphous substances.

In accordance with the problem considered by us, the following moments are important. First, the most of the objects under study, which are called amorphous, have the parameter $e(p,T) \ll 1$ and demonstrate quite high thermal and time stability of the atomic structure. Second, the experimental data available now do not indicate the possibility of pointing out the additional aggregate states on the basis of the $e(p,T) \ll 1$ criterion. Third, the transition to the solid state is, in general case, possible both from the region of the aggregate state of the gas and from the liquid aggregate state (fig. 1). Fourth, the change of the external conditions of transition from one aggregate state to another one affects considerably the structure and the properties of the final substance produced. Simultaneous account of these moments, in our opinion, results in a clear conclusion: the amorphous substances are realized in the solid-state region of the phase diagram, i.e. they are attributed to the solid aggregate state. In this relation, for example, it makes no sense to treat the glass as the liquid, even the super-cooled one. The $e(p,T)$ criterion indicates clearly the necessity to relate the glass to the solid aggregate state [1]. Though by their structure the glasses are similar to liquids, by the interaction force and by the character of thermal movement of the structural particles they are typical solids. The lack of the translation movement of the structural particles and conservation of, primarily, their oscillations only around the equilibrium positions are common for both the crystalline and the amorphous states. In this case the main problem that stipulates the transition of the liquid to the ordered crystalline or unordered amorphous state is the character and the value of the strength of the chemical bonds between the structural particles.

Thus, different phases could be realized in the solid-body field of the phase diagram for specific substance dependent of the conditions of production of the above substance. In equilibrium conditions, this field is filled with the polymorph crystalline modifications, for example, the α-phase, β-phase and γ-phase (fig. 1). In the non-equilibrium or quasi-equilibrium synthesis conditions, the glassy, amorphous, nanostructural and other disordered phases occurring at the same temperatures and pressures as the crystalline ones may be realized in this field [2, 3, 4]. The occurrence of different unordered phases in fig. 1 is indicated by the bands separated by the dotted curves. As seen from figure 1, not only the crystalline but also the structurally unordered amorphous substances may correspond to the α-, β- and γ-phases [5].

The transition of available non-equilibrium unordered solid phases to the equilibrium ones is possible only in case of the discrete leap-like change of different parameters (volume, entropy, enthalpy etc.), i.e. due to the phase transitions of the first kind. The peculiarity of this transition is that after the completion of the above transition the final state of the substance is located at the same point of the $p–T$ diagram as the initial one. These states differ by the character of the atomic network structure and by the degree of non-equilibrium. In Ref. [6], the possibility of the transitions from the ordered (crystalline) phase to the unordered (amorphous) phase with increasing pressure of the system is specified.

Another approach to classification of the substances based on their atomic and molecular structure [2] is important in the modern physics. According to it, the terms 'ordered' and 'unordered' must occupy the next hierarchic level [7]. This hierarchic level is typical for any aggregate state. This term most frequently means the presence or the absence of deviations with respect to the certain parameter(s) as compared to the system that serves the reference of particular ordering and is called the ideal system [8]. In this case the classification lies between two boundary cases: the ideal reference completely ordered system (e.g., ideal crystal) and the ideal reference completely disordered system (e.g., ideal gas). Correspondingly, the terms 'ordered' and 'unordered' could be applied to any system, which has total or partial ordering or disordering at least by one parameter as compared to the ideal structure. Thus, in general case, the gases (plasma), liquids, and solids could be both ordered and disordered by some parameters, occupying certain intermediate state between the ideal boundary cases. Regarding the solids, it should be noted that their division by the structural peculiarities into the crystalline (with the ordered structure) and amorphous (with the unordered structure) is generally accepted [9] and is based on the results of the contemporary complex structural studies [2].

Thus, the parameter $e(p,T)$ and the degree of the structural ordering correspond to the two different levels and two substantially different views of classification of the substances [10]. Therefore, the aggregate state of the solid must combine two large classes of the substances: the ordered solids and the unordered solids. Such division into the above classes must be made not in the plane of their assignment to the certain aggregate state, but in the plane of the specific peculiarities of the atomic structure and physical and chemical properties. It is assumed here that the crystals are the ordered solids, whereas the amorphous substances are the unordered solids. However, in this case non-ordering does not mean a total chaos in the atomic locations [11]. As J. Zaiman [12] expressly noted, the term 'disordering' in this context means the presence of a 'violated order', not the total order. What order is violated in the amorphous substances, what order do the 'miss'? In our opinion, the reference point should be specified by the reference system of the ideal order in the solid. The simplest and the most general parameter of the occurrence of disordering in this system is SRO.

Thus, taking into account the above analysis, it should be stated that one of the principal classification criteria of pointing out the class of the unordered substances among the solids is the lack of long rangr order (LRO) in their structure [13]. Such classification corresponds to the hierarchic level next after the aggregate state. Two groups of identical terms are 'located' on this level. The first group includes the 'disordered solids' or the 'crystalline substances'/crystals. The second group combines the 'unordered solids' or the 'non-crystalline'/'amorphous' substances [14, 15]. The solids with LRO belong to the first group, whereas those without LRO enter the second group.

In this context, the following comments seem to be important. First, application of the above two groups of terms should not go beyond the same aggregate state of the substances, for instance, the solids [16]. Second, one has to keep in mind the ordering (or disordering) not by any structural parameter, but only by the character of mutual topological spatial geometric locations of the structural particles. That is, the single parameter used to estimate ordering or disordering on this level is the topological LRO only. Third, if one takes into account the two first conditions, we don't see the essential reasons to consider the term 'non-crystalline' substance more general than the 'amorphous' substance.

Note V.S. Minaev's sensible comment [17]: rigorous etymological value of the terms 'amorphous' and 'disordered' means total, not partial, absence of the shape and order, i.e. both notions include the meaning of the lack of any order. Therefore V.S. Minaev assumes that generally accepted term 'amorphous' should be replaced by 'semi-amorphous', while 'disordered' – by 'semi-disordered'. Having completely agreed with these comments, we, nevertheless, see no necessity in the replacement of generally accepted terminology. However, regarding the solids, the total lack of the topological LRO should be taken as the only basis of etymological meaning of the terms 'amorphous', 'unordered' and 'disordered'. Therefore, further the term 'ordered' state should define the substances with total topological order that necessarily includes the topological LRO as well, while the 'unordered' state – the substances with no topological LRO in the structural particles location. As regards the substances with no topological order, they will be specially denoted by the term 'totally disordered state'.

It is unreasonable to extend the area of application of the term 'amorphous substance' to the liquids [16, 18]. Ordering or disordering is a typical attribute of the condensed state in general. In this relation, we may refer to Ref. [14], which clearly states that the liquids could be disordered (common) and ordered (e.g., liquid crystals and polymers) as well. A particular, well-developed system of terms does exist to describe the liquids as the specific aggregate state. In some cases of ordering in the liquids in the LRO scale, the special terms, for example, the 'liquid crystals', are used. Thus, the terms 'disordered' and 'unordered' could, in our opinion, be applied both to the liquids and solids. The term 'amorphous', in turn, is applicable only for the solid condensed systems, since the liquids have no shape due to their physical and chemical nature.

Thus, the term 'amorphous' concerns the solid aggregate state of any substance having no topological LRO, i.e. the structure of which could not be described by a certain spatial lattice with the translation symmetry. We shall call the lack of the topological LRO the disordering (or non-ordering). Therefore, if we deal with a solid aggregate state, the terms 'amorphous', 'non-crystalline', 'unordered' and 'disordered' can be considered equivalent and used as synonyms. In the same context, the terms 'crystalline' and 'ordered' for the systems with the topological LRO can be considered synonyms as well.

Thus, all the substances during their phase transition from the gaseous or liquid state to the solid state could be realized in a form of the unordered (amorphous) systems with no topological LRO, or as the ordered systems (crystals) with topological LRO. In certain conditions, the transitions between the above kinds of the solid state are also possible. In case of the transitions 'crystal → amor-

phous body' LRO vanishes, while at the transitions 'amorphous body → crystal' LRO arises.

In many cases there is no clear boundary between the crystals and amorphous materials [13]. For instance, in the crystal with high defect concentration the regular atomic structure may be violated resulting in LRO breakage or even vanishing. Increase of the defect concentration leads in this case to the crystalline lattice destruction and, as a result, to the continuous transition of the crystalline state to the amorphous one. In addition, both the crystalline and amorphous states may have different ordering degree.

The next, lower, step of the hierarchic pyramid contains the terms that define different classes/kinds of the amorphous substances, each of them having specific characteristics of the atomic network disordering, not inherent in other ones. The examples are the glasses, amorphous films, amorphized solids, gels, pastes etc. In each of these classes, the principal question is the relation between the order and disorder.

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Боркач Е.И., Иваницкий В.П., Ковтуненко В.С. Аморфное состояние в иерархической классификации вещества
Аннотация. Аннотация. Лежащее в основе выделения разных агрегатных состояний веществ соотношение средней кинетической энергии движения структурных частиц к средней потенциальной энергии их взаимодействия указывает на однозначную реализацию аморфных веществ именно в твердотельной области фазовой диаграммы. При равновесных условиях получения эту область заполняют полиморфные кристаллические модификации, а при неравновесных условиях в эту же область попадают различные стеклообразные, аморфные и другие структурно неупорядоченные фазы. «Упорядоченным» или «неупорядоченным» по определенному физическому параметру может быть любое агрегатное состояния вещества. При этом степень разупорядочения определяется дисперсией распределения величины одного параметра или нескольких параметров системы. В соответствии с этим и твердотельное агрегатное состояние объединяет в себе два больших класса веществ: упорядоченные твердые тела (в основном это кристаллы) и неупорядоченные твердые тела (или аморфные вещества). При этом основными параметрами такого разделения являются геометрические характеристики пространственного расположения структурных частиц вещества между собой, что определяет топологический порядок твердого тела. Таким образом, термины «розупорядоченное» или «неупорядоченное» можно применять для любого агрегатного состояния веществ, а термин «аморфное» – только для твердотельных систем. В более узком смысле слова аморфным является твердотельное агрегатное состояние любого вещества, в котором отсутствует топологический дальний порядок, то есть структуру которого нельзя описать пространственной решеткой с определенной группой симметрии.
Ключевые слова: агрегатные состояния веществ, фаза, аморфные вещества