Pressure-temperature phase diagrams of selenium and sulfur in terms of Patashinski model

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Abstract

The pressure-temperature phase diagrams of Se and S are calculated. Both melting and polymorphous phase transitions are described in frames of statistical Patashinski model. The results are in good agreement with experimental data of Brazhkin et. al.

Keywords: Patashinski model, phase diagram, selenium, sulfur.

1 Introduction.

Structural transitions in liquid Se and S similar to those in crystalline state were discovered by Brazhkin et.al. [1]. At these transitions, drastic changes of structure and physical properties (electrical conductivity, heat capacity, etc.) occur [2]. Actually, the pressure-temperature phase diagrams of these substances demonstrate two kinds of phase transitions. The first one corresponds to the sharp change of local order in the system. In solid state, these transitions are known as polymorphous ones. The possibility of polymorphous transitions in liquid area is under permanent discussion. Another kind of transitions, i.e. melting, is associated with global order changes. To describe the phase diagram, one has to describe both transitions in terms of one and the same statistical model or, in other words, one has to describe all phases of the system in terms of one and the same set of order parameters. Such a description may be realized via local state representation in statistical mechanics of condensed matter introduced by Patashinski [3]. The idea that local state representation may describe the liquid-liquid phase transition was suggested in [4], and we tried to realize it in the present paper. Here, we give brief introduction into Patashinski model (section 2), then we perform calculations for the system with two competing local structures. The results are applied to the binary system and to the system with two polymorphous local modifications, such as Se and S (section 3). Further applications of the model are discussed in Conclusion.
2 Patashinski model.

Physical background of the model arises from the fact that in condensed substance the interaction on atomic length-scale is strong enough to result in a substantial restriction of relative positions of particles. This is being referred to as the local order in condensed systems. The size of strongly correlated clusters and the nature of local order depends on the temperature, pressure, and composition of the material. The local ordering implies that atoms positions in the local cluster correspond to some deformed ideal pattern. In close-packed materials, one supposes several geometrical objects (the fragments of HCP and FCC lattices and icosahedron) to be such a pattern. The pattern can be characterized by geometric parameters which are invariant under rotations (coordination lengths and numbers, characteristic angles in the pattern). These parameters are the same for most clusters and fix up the type of local order in the material.

To account the limitations imposed on relative positions of particles by the local order, one describes the system in terms of local order parameters. Since the concept of local order assumes a space scale larger than mean interatomic distance, a coarsening of the description is necessary. The resulting model is then a simplification that allows one to understand global ordering starting from the assumed local order and from the interaction of local orders in different clusters. The formalism considered was first offered by A. Patashinski and M. Chertkov in [3], and below in this section we will follow this paper.

As was discussed above, material is treated as a system of small clusters of equal size, each cluster being in one of a set of $N$ local structural states. The same set of local states is assumed for all clusters; a number $i = 1, N$ is assigned to each of the states of this set. A state of the whole material is then described by the field $\sigma_i(r)$, where $\sigma_i(r)$ is an $N$-component vector defined by the rule: $\sigma_i(r) = 1$, if the state of the cluster placed at point $r$ has number $i$, and $\sigma_i(r) = 0$ in other case. To proceed with a statistical theory of the local and global order, one has to find the non-equilibrium free energy (effective Hamiltonian, [5]) as a function of the configuration $\{\sigma_i(r)\}$. One expects the effective Hamiltonian $H\{\sigma\}$ to include independent contributions from different clusters, and interaction energy that depends on the states of more than one cluster:

$$H\{\sigma\} = -\sum_{r,r'} \sigma_i(r) M_{ij} (r - r') \sigma_j(r') - \sum_r \sigma_i(r) a_i(r)$$

Here and below, the Einstein’s summation rule is supposed. In (1), $a_i$ is internal energy of a cluster having state number $i$, and interaction energy is written as two-cluster interaction of general form. Free energy (1) defines the order parameter field

$$<\sigma_i(r)> = w_i(r) = \frac{1}{Z} \sum_{\{\sigma\}} \sigma_i(r) \exp\left(-\frac{H\{\sigma\}}{T}\right),$$

$$Z = \sum_{\{\sigma\}} \exp\left(-\frac{H\{\sigma\}}{T}\right)$$

(2)
Here, the partition function $Z(\alpha_i(r), T)$ is a sum over all local states. As can be seen from (2), the $\omega_i(r)$ is the probability of state numbered by $i$ to occur at point $r$, and

$$\sum_{i=1}^{N} w_i(r) = 1. \tag{3}$$

Partition function $Z$ may be treated as generating functional for the order parameter field $w(r)$:

$$w_i(r) = \frac{\delta \ln Z}{\delta \alpha_i(r)}. \tag{4}$$

To calculate $Z$, one uses Hubbard - Stratonovich transformation. Namely, let us suppose that the quadratic form in Hamiltonian is positively defined, and its kernel may be written in the form:

$$M_{ij}(r) = E_{ij} J(r) \tag{5}$$

(As it will be shown below, this is not relevant for the mean field approximation).

Introducing real $N$-component "conjugated" field $\psi_i(r)$, one rewrites $Z$ as

$$Z = \int \prod_{i,r} D\psi_i(r) \exp\{-\frac{1}{T} \sum_{r,r'} J^{-1}(r-r') E_{ij} \psi_i(r) \psi_j(r')\} \times \prod_{i,r} Tr \exp\{\frac{1}{T}(E_{ij} \psi_i(r) \sigma_j(r) + \alpha_j(r) \sigma_j(r))\}. \tag{6}$$

Here, the integration $D\psi$ goes over all components $\psi_i$ of the field $\psi(r)$ in each point $r$. In (6), the summation over local states can be easily done:

$$Z = \int \prod_{i,r} D\psi_i(r) \exp\{-\frac{F}{T}\},$$

$$F = \frac{1}{T} \sum_{r,r'} J^{-1}(r-r') E_{ij} \psi_i(r) \psi_j(r') - T \sum_r \ln[\sum_i \exp\{\frac{1}{T}(E_{ij} \psi_j(r) + \alpha_j(r))\}]. \tag{7}$$

In this relation, $\psi_i(r)$ is a continuous variable, so one is able to apply well-known method of analysis - to find out the most probable configuration which minimizes the thermodynamic potential, then to investigate fluctuations around it, etc. Here, we shall restrict ourselves with the first step, which is the mean field approximation (MFA).

Function $\psi(r)$, which minimizes the thermodynamic potential $F$ in (6) (most probable configuration) obeys following equation:

$$\sum_{r'} J^{-1}(r-r') \psi_i(r') = Z_0^{-1} \exp[\frac{1}{T}(E_{ij} \psi_j(r) + \alpha_j)],$$

$$Z_0 = \sum_i \exp[\frac{1}{T}(E_{ij} \psi_j(r) + \alpha_j)]. \tag{8}$$

Substituting solution of this equation into (6), and using relation $F(\psi) = -T \ln Z$, one gets the generating functional $Z$. The probability $w_i(r) = -\delta F/\delta \alpha_i(r)$ coincides then with the right side of (3). Then, for $w_i(r)$, one has

$$w_i(r) = \langle \sigma_i(r) \rangle = \sum_{r'} J^{-1}(r-r') \psi_i(r'). \tag{9}$$
The \( F \) is similar to nonequilibrium thermodynamic potential in the Landau theory, with order parameter \( \psi^\alpha(r) \). At equilibrium, \( F \) is minimal. Let us define \( w_i(r) \) for nonequilibrium \( \psi \) using (9). Now the nonequilibrium potential \( F \) may be written in terms of \( w_i(r) \):

\[
F = \frac{1}{2} \sum_{r,r'} M_{ij}(r-r')w_i(r)w_j(r') - \frac{1}{T} \sum_r \ln[\sum_i \exp\left(\frac{1}{T}(\sum_r M_{ij}(r-r')w_j(r') + \alpha_i)\right)].
\]  

(10)

As can be seen from (10), condition (5) is not essential in MFA. The nonequilibrium thermodynamic potential written in terms of order parameter field \( w_i(r) \), is the base of Landau-like theory. At equilibrium, one has

\[
\frac{\delta F}{\delta w_i(r)} = 0,
\]  

(11)

with normalizing condition (3). In explicit form, this equation may be written as

\[
w_i(r) = Z^{-1}(r) \exp\left(\frac{E_i(r)}{T}\right)
\]

\[
E_i(r) = \sum_{r'} M_{ij}(r-r')w_j(r') + \alpha_i(r)
\]

\[
Z(r) = \sum_{i=1}^N \exp\left(\frac{E_i(r)}{T}\right).
\]  

(12)

Here, the \( E_i(r) \) may be understood as the energy of cluster having local state number \( i \), while the states of surrounding clusters are characterized by the mean probability \( w_j(r') \). If the field \( \alpha \) depends no on spatial coordinates, \( \alpha(r) = \alpha(0) \), then \( E_i, w_i \) are spatially homogeneous too:

\[
E_i = M_{ij}w_j + \alpha_i, \quad M_{ij} = \sum_r M_{ij}(r).
\]  

(13)

The normalizing condition (3) is fulfilled for solutions of (12) automatically. Depending on parameters of the theory \( (M_{ij}, \alpha_i, T) \), equations (12) may have a set of solutions. In the vicinity of the first order phase transition, one expects at least two minima of \( F \), corresponding to stable and metastable phases. The lowest minima corresponds to the stable one. As an example of application of formalism described, let us consider \( N \)-local states model with special interaction:

\[
M_{ij} = J\delta_{ij}, \quad \alpha_i(r) = 0
\]  

(14)

which is the Potts model \( \delta \). In \( \delta \), the Potts model was applied to describe the melting of a single-component material. The set of local states in this case should be understood as a set of allowed orientations of local clusters. The
physical picture is that each cluster of condensed material may be treated as a
deformed cluster of ideal crystal. It is obvious for crystal phase; For liquid, this
statement is an assumption, which seems to be correct for a wide range of
materials. For locally crystalline material, one studies the statistics of orienta-
tions of local anisotropy. To obtain the effective Hamiltonian of orientational
degrees of freedom, one uses following considerations. If two clusters share a
boundary, then the minimum of their interaction energy corresponds to the co-
cinciding of their orientations. If the minimum is deep enough, then one is able
to divide the space of orientations in equal cells and to use a coarsened descrip-
tion of orientations in terms of orientation cells. The number of cells has to be
chosen as to comprise the orientation attraction region, where the interaction
energy is close to its minimum. Denoting the depth of the minimum as \( J \), and
the number of cells as \( N \), one arrives at the effective Hamiltonian (14) of the
Potts model which behavior is known. At low temperatures, the material is
orientationally ordered: all clusters with probability \( \approx 1 \) have one and the
same orientation (crystal). At high temperatures, all orientations are of equal
probability (liquid). The melting of the material is therefore described as an
orientation disordering. More detailed microscopic consideration of the relation
between the Potts model and melting may be found in [8]. Note that an appro-
priate choice of two phenomenological parameters \( J, N \) makes it possible do
relate correctly several quantities, such as melting temperature, spinodal tem-
peratures, the hidden heat of transition, heat capacity jump. That is more than
one would expect from such a simple model.

The melting theory, based on the Potts model, and our further considerations
essentially deal with the statement that the local order does not change via
melting - the same set of ideal patterns may be assigned to the liquid and to
the crystal. This statement has no universal character, this is suggestion. In
some cases, inherent amorphous structures may be involved during melting [9].
But for systems considered, there exist supportive arguments for the crystalline
local structure both in the crystal and in the liquid [3].

3 System with two competing local structures

In this section, we discuss an idealized model of a material having two possible
local structures. Each structure has its own set of allowed orientations. One
introduces two indexes to enumerate the local states:

\[
\sigma^i_k; \quad i = 1, 2; \quad i = 1 \rightarrow k = 1, n; \quad i = 2 \rightarrow k = 1, m.
\]  

(15)

The upper index corresponds to the type of local order, while the lower one
enumerates the orientations. The first and the second structures have \( n \) and \( m \)
allowed orientations respectively. If only two-cluster interactions are accounted,
then Hamiltonian takes the form

\[
-H = \alpha \sum_i \sum_{r} \sigma^i_1(r) + \sum_{r, r'} \sum_{r, r'} \sigma^i_1(r) M_{kl}^{ij}(r - r') \sigma^j_l(r'),
\]  

(16)
where $\alpha$ is the difference of internal energies of two local structures. The kernel of interaction differs from zero only for nearest neighbors. We suppose it may be written in the form:

$$
M_{kl}^{11} = \tilde{J}_1 \delta_{kl}; \quad M_{kl}^{22} = \tilde{J}_2 \delta_{kl}; \quad M_{kl}^{12} = M_{lk}^{21} = \tilde{\varepsilon} \tag{17}
$$

Such a form of interaction arises from following. Let the two structures differ sharply from each other. If two clusters with different structures share a boundary, then their interaction energy is $\tilde{\varepsilon}$ despite of their orientations; the orientational interaction of neighbors having one and the same local structure is described by the Potts model. Parameters $\tilde{J}_1, \tilde{J}_2$ are the depths of orientational interaction of structures 1 and 2 respectively, and $\tilde{\varepsilon}$ - is an interstructural surface energy. Following notations will be used below:

$$
\varepsilon = \tilde{\varepsilon} \nu; \quad J_1 = \tilde{J}_1 \nu; \quad J_2 = \tilde{J}_2 \nu, \tag{18}
$$

were $\nu$ is the number of nearest neighbors.

For the mean-field order parameter, one supposes, in analogue with the Potts model:

$$
\begin{align*}
    w_1^1 &= w_1; \quad w_{k \neq 1}^1 = \frac{p - w_1}{n - 1} \\
    w_1^2 &= w_2; \quad w_{k \neq 1}^2 = \frac{1 - p - w_2}{m - 1}.
\end{align*} \tag{19}
$$

Here, $p$ is the mean probability of the first structure. Relations (19) realize the idea of orientational ordering; the number 1 is assigned to the orientation which is most probable in the crystalline state. Now one is able to introduce following classification of possible phases in the model:

1. $w_1 \sim p, \ p \sim 1$ - crystal with the first type of local structure;
2. $w_1 = p/n, \ p \sim 1$ - liquid with the first type of local structure;
3. $w_2 \sim 1 - p, \ p \sim 0$ - crystal with the second type of local structure;
4. $w_2 = (1 - p)/m, \ p \sim 0$ - liquid with second type of local structure;

For the thermodynamic potential (10) per one cluster, one gets

$$
\begin{align*}
    f &= - J_2 (1 - p)^2 \left( \tilde{w}_2 - \frac{\tilde{w}_2^2}{2} - \frac{(1 - \tilde{w}_2)^2}{2(m - 1)} \right) \\
    &\quad - J_1 p^2 \left( \tilde{w}_1 - \frac{\tilde{w}_1^2}{2} - \frac{(1 - \tilde{w}_1)^2}{2(n - 1)} \right) \\
    &\quad - \varepsilon p (1 - p) + T (1 - p) \ln (1 - p) + T p \ln p \\
    &\quad + T p \ln \tilde{w}_1 + T (1 - p) \ln \tilde{w}_2 + p \alpha, \tag{20}
\end{align*}
$$
where the values $\tilde{w}_1 = w_1/p$, $\tilde{w}_2 = w_2/(1 - p)$ obey equations

$$\tilde{w}_1 = \left[ 1 + (n-1) \exp \left( \frac{J_1 p (1 - n \tilde{w}_1)}{T(n-1)} \right) \right]^{-1}, \quad (21)$$

$$\tilde{w}_2 = \left[ 1 + (m-1) \exp \left( \frac{J_2 (1 - p) (1 - m \tilde{w}_2)}{T(m-1)} \right) \right]^{-1}. \quad (22)$$

With the help of (20), the phase diagram of the model can be plotted in MFA for two physically different cases, considered below.

The first case is binary system in which the second type of local order occurs due to presence of second component, i.e. the binary system with limited miscibility of the components. The two types of local order correspond to the pure substances $A$ and $B$. The model can be applied to systems in which the two types of local order differ sharply (have different groups of local symmetry or incompatible interatomic distances). In detail, the calculations are performed in [10], where it was shown that all types of phase diagrams for binary systems with limited miscibility of the components (eutectic and monotectic ones) are described correctly. To demonstrate validity of the model, we calculated the concentration - temperature phase diagrams for well known binary systems Ga-Pb and Ag-Cu. The results are plotted on fig.1. One can see some deviations from experimental data published by Elliott [11]. Determination of model parameters was made by following way. The parameters are $J_1, n, J_2, m, \alpha, \varepsilon$. Parameters $J_1, n$ and $J_2, m$ correspond to pure components and were determined from the heat capacity temperature dependencies of pure Ag, Cu, Ga, Pb [12]. For binary system, where the concentration of second component is an external parameter, the value of $\alpha$ does not play any role: it should be chosen as to provide the fixed concentration of mixture. The only parameter to fit known diagram is $\varepsilon$! Thus, the agreement with the experiment is rather good.

For the Ag-Cu system the parameters are : $J_1 = 1.356$, $n = 4$ (Cu), $J_2 = 1.234$, $n = 4$ (Ag), $\varepsilon = -0.275$. The Ag melting temperature was chosen as the unity. For Ga-Pb, the parameters are $J_1 = 3.18$, $m = 11$ (Pb), $J_2 = 1.6, n = 11$ (Ga), $\varepsilon = -1.596$. Temperature unity corresponds to the Ga melting point.

### 4 Selenium and sulfur.

Consider now the system where atoms rearrangement changing the type of local order in small cluster is allowed. Instead of binary system, one has the substance with polymorphous modifications. The thermodynamic potential (20) may be applied to plot the phase diagram also. Phase transitions arise, if one changes the model parameters - $J_1, J_2, \alpha, \varepsilon$. In physical situation, the change of parameters may occur under pressure. Here, we describe the pressure - temperature phase diagrams of Se and S which are known experimentally [2]. The coefficients in the model were chosen as to fit the experiment. The calculations are presented at fig.2, fig.3. For sulfur, the calculations were done by following way. First, the
parameter \( n \) (number of orientations of low-pressure structure) was determined from the heat capacity data for melting at atmospheric pressure. Since there is no reliable heat capacity data for high-pressure structure, the parameter \( m \) was supposed to be near 4. We suggest this value because of our experience in similar calculations: for systems with high density, the number of orientations tends to two “magic” values, 4 or 11. In our case, the value 4 provides better correspondence to experiment. We suppose linear pressure dependence for \( J_1, J_2, \alpha \) and no pressure dependence for other parameters (\( n, m, \varepsilon \)). The coefficients in linear dependencies \( J_1 = a_1 p + b_1, J_2 = a_2 p + b_2, \alpha = a_3 p + b_3 \) were determined from the “tales” of experimental diagram: \( a_1, b_1 \) - from the low temperature and low pressure line between phases 1 and 2, \( a_3, b_3 \) - from the interphase line near critical point, \( a_2, b_2 \) - from the melting line at high pressure. The central part of the diagram was then plotted automatically. For sulfur, the parameters are \( n = 2.5, m = 4, a_1 = 0.527, b_1 = 2.433, a_2 = 0.558, b_2 = 3.296, a_3 = -0.094, b_3 = 1.535, \varepsilon = -4.506 \). One can see good correspondence between calculations and experimental data. At higher temperatures, there exist another phase transition into metallic liquid, but it is out of our consideration.

For selenium, the calculations were done by similar way. The only difference is that the position of melting line at high pressure is not known from experiment, so we tried to reproduce the interphase line between crystal phases at low temperatures, which position on the diagram was supposed by V. Brazhkin. So, the correspondence to the experiment in the case of Se allows to wish better. The parameters for selenium are \( n = 2.5, m = 4, a_1 = 0.623, b_1 = 2.433, a_2 = 0.443, b_2 = 1.3, a_3 = -0.226, b_3 = 1.145, \varepsilon = -4.133 \).

In both cases, temperature scale was chosen as to make the melting temperature at atmospheric pressure equal to unity.

5 Conclusion

The main advantage of the model considered is the fact that all possible phases are described by one and the same order parameter - vector of mean probabilities. This gives one possibility to write out the expression for thermodynamic potential which is valid for all situations, and thus to investigate the phase transitions.

In the model, the drastic changes of structure in liquid are described as the continuation of the line of polymorphous phase transition into the liquid area, where it terminates in the critical point. Below critical temperature, the two types of local order are well distinguished, and phases 2 and 4 (see classification) are divided by the line of the first order phase transitions. At critical temperature, the transition is of second order. Above it, the local structures are degenerated by thermal fluctuations. Note, that the well-known phase diagrams at fig.1 and phase diagrams presented at fig.2, fig.3 are the diagrams of one and the same model. The only difference is that for fig.2, fig.3 one uses pressure instead of concentration as a thermodynamic parameter.

Further application of the model concern an interesting line corresponding to
the equilibrium of liquid and crystal having different types of local order (phases 1 and 4). We hope the model to explain "anomalous" melting of covalent crystals with diamond structure (C, Si, Ge) and compositions of type $A_{111}B_5$ (In-Sb, Ga-Sb) with zincblende structure. Melting of these substances is accompanied with changing of the type of chemical bonds and sharp changing of local order (coordination number rises approximately in two times) \[13, 14\]. This results in essential increasing of density and in the semiconductor - metal transition during melting \[13\]. At the same time, at high pressures, these substances transform into metallic crystals with the structure of white Sn \[15\]. One can say that there exist a line of semiconductor - metal transition which changes its direction at the crossing point with the line of metal crystal melting. This point is the point of three - phase equilibrium of covalent crystal, metallic crystal, and metallic liquid. In principle, the line of coexistence of crystal and liquid with different local structures may terminate at lower pressure in the crossing point with the line of covalent crystal - covalent liquid transition. Then the line of polymorphous transition should be plotted into the liquid area and terminated in the critical point. For substances mentioned, this is doubtful because the "covalent" melting should take place at large temperatures \[16\]. It is more reliable that the line terminates near the liquid - gas equilibrium, which is out of the validity of the model due to the destroying of local order at high temperatures.

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Figure 1: Temperature - concentration phase diagrams of Ag-Cu and Ga-Pb binary systems. Solid lines represent experimental data [11], while the dashed ones correspond to our calculation.
Figure 2: Pressure - temperature phase diagram of sulfur. Solid circles represent the experimental data, solid lines correspond to our calculation. Critical point is shown as an empty circle. The enumeration of phases corresponds to the classification given in the text.
Figure 3: Pressure - temperature phase diagram of selenium. Solid circles represent the experimental data, solid lines correspond to our calculation. Critical point is shown as an empty circle. The enumeration of phases corresponds to the classification given in the text.