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15 The Void Concept for Phase and Glass Transitions in Clusters

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I've given up trying to be rigorous. All I'm concerned about is being right

Steven Hawking

Abstract

Configuration excitations of clusters with pair interaction between atoms result in formation of internal voids for bulk and very large clusters and surface voids for not too large clusters. The liquid state of these clusters is a configurationally excited and thermodynamically stable state, while the glassy-like state is thermodynamically unstable state, i.e. it is an excited state with frozen-in voids. It is shown that it is a contribution of thermal oscillations of atoms to the entropy of the liquid state that leads to a widely correct interpretation of experimental results on melting by the Lindemann criterion for melting, although the basic assumption underlying the Lindemann criterion is not correct. As for the glassy-like states of bulk rare gases, which are in reality the result of evolution of the liquid state to low temperatures below the freezing point, the role of thermal oscillations of atoms is not significant.
15.1 Introduction

We consider systems of bound atoms with a pair interaction between them, both bulk systems and clusters, i.e. systems containing a finite number of atoms. There are two types of excitations of these systems, configuration excitation and that due to thermal motion of atoms or phonon excitation. Assuming existence of two states of aggregation of these systems, the solid and liquid ones, we find that the configuration excitation is responsible for the phase transition solid-liquid in these systems of bound atoms. The nature of configuration excitation can be added to the thermodynamical description, that consists in formation of vacancies or voids [1], and this character of excitations allows us to analyze the properties of the states of aggregation in detail. In particular, the liquid state corresponds to a minimum of the free energy as a function of the excitation energy, and this state of aggregation exists in this form up to the freezing temperature, i.e. below this temperature the configurationally excited state of the bulk system becomes unstable. The decay of such a state of a bulk system results in diffusion of voids to its boundary, or vice versa. Because this process has a barrier character and its rate decreases sharply with a temperature decrease, this excited state can be a frozen-in liquid state, i.e. this configurationally excited state is an analogue to glassy states. We call these states with frozen-in voids as glassy-like states of systems of bound atoms.

Since the liquid and glassy-like states of a system of bound atoms with pair interaction are configurationally excited states of this system, one can analyze these states from a general point of view. Such an analysis is the goal of this paper. In considering these systems, we are guided by bulk and clusters of rare gases and use the parameters of real rare gases for determination of parameters of configuration excitation of the systems. The results of computer simulations of clusters are of importance for this analysis as well.

This consideration of clusters can be combined with the saddle-crossing analysis of clusters [2, 3, 4, 5]. Indeed, the potential energy surface (or the potential energy landscape) for clusters with a pair interaction of atoms has a large number of local minima at zero temperature in space of atomic coordinates [6, 7, 8, 9, 10], and these local minima are separated by barriers or saddle points. Each local minimum corresponds to a certain configurational excitation of a cluster. During the evolution at low temperatures, a cluster is found mostly in local minima of the potential energy surface, and intermediate states are realized for short times. Combining this consideration with the void concept of cluster configuration
excitation, one can define the cluster state of aggregation as a group of configurationally excited states with near excitation energies, where each excitation state corresponds to a cluster location at a certain local minimum of the potential energy surface. Within this definition, each cluster state of aggregation is characterized by a certain energy and entropy, and in the limit of large cluster sizes this description leads to the respective results known from classical thermodynamics.

Taking the nature of the phase and glassy transition for clusters and bulk systems of bound atoms as a result of change of their configuration state, we ignore the role of thermal motion of atoms. In contrast to this, the Lindemann criterion for the phase transitions [11, 12] takes thermal oscillations of atoms as the basis origin for the phase transition. We show below on some examples that thermal motion of atoms influences these phenomena indirectly. Indeed, configuration excitation of clusters facilitates the motion of atoms at finite temperatures by an increase of the size of the accessible region for atomic motion. This gives a remarkable addition to the entropy of a configurationally excited state at the melting point, so that thermal motion of atoms changes significantly the parameters of the phase transition. Therefore, though the idea of the Lindemann criterion is not valid basically, this criterion reflects correctly the tendency in this phenomenon. For glassy-like states which are realized at low temperatures, the role of thermal motion of atoms is weaker.

Thus, configuration excitation of bulk systems of bound atoms with pair interactions result in formation of internal voids, and their parameters can be found from parameters of the liquid states of rare gases. In contrast to bulk systems, configuration excitation of not so large clusters follows from the formation of surface voids, and information about parameters of these voids is connected with the results of computer simulations of clusters. Below we analyze these systems from a general point of view.

15.2 States of Aggregation of Clusters

According to the definition, a state of aggregation of a bulk system of bound atoms corresponds to a thermodynamically stable and spatially uniform distribution of atoms. It is clear that the ground state of a system of bound atoms is the crystalline state. Then the liquid state of this system corresponds to other configurations of atoms.

From the microscopic point of view, we define a state of aggregation as a group of atomic configurations with near energies of excitation and a high total entropy.
Thus, we will consider the state of aggregation of a system of bound atoms as a configuration excitation of the ground state of this system and will characterize this state by a certain excitation energy, $\Delta E$, and statistical weight, $g$, with respect to the ground state. This procedure is applicable both to bulk systems and clusters.

Then introducing the entropy of this state of aggregation $\Delta S = \ln g$, one can construct the free energy of this state $F$ with respect to the ground state

$$ F = \Delta E - T \Delta S, \quad (15.1) $$

where $T$ is the temperature. The condition $F = 0$ gives us the temperature $T_m$ of the phase transition between the ground and excited states of aggregation

$$ T_m = \frac{\Delta E}{\Delta S} = \frac{\Delta E}{\ln g}. \quad (15.2) $$

Restricting the consideration to two states of aggregation of a system of bound atoms, one of those being the ground state, we have the approach of two aggregate states [13]. By definition, we will call the ground state of a system of bound atoms the solid state, and the excitation aggregate state of this system the liquid state.

Let us introduce the probabilities for a system to be found in the solid, $P_{sol}$, and liquid, $P_{liq}$, states to be equal to [13, 14, 15]

$$ P_{sol} = \frac{1}{1 + g \exp\left(-\frac{\Delta E}{T}\right)}, \quad P_{liq} = \frac{g \exp\left(-\frac{\Delta E}{T}\right)}{1 + g \exp\left(-\frac{\Delta E}{T}\right)}. \quad (15.3) $$

As it is seen, in this approximation we ignore intermediate excited states of a system of bound atoms.

Above relations give a phenomenological description of aggregate states of a system of bound atoms with finite and infinite numbers of atoms. We analyze, now, the problem from another point of view, considering various configuration excitations of a system of bound atoms as local minima of a potential energy surface of this system. The number of local minima of the potential energy surface is high even for small clusters and grows exponentially with increasing cluster size [7, 8, 9]. Hence, the development of a system of bound atoms as a result of motion of this system along the potential energy surface is determined by a passage via saddles and local minima of this potential energy surface [2, 3, 4, 5, 16]. Thus,
the general character of transitions in clusters between different states of configuration excitation consists in transitions between local minima of the potential energy surface with overcoming of barriers which are saddle points of the potential energy landscape and separate neighboring local minima. This character of cluster evolution, the so-called saddle-crossing dynamics [4], leads to the conclusion that most of the time the cluster is found in local minima of the potential energy landscape, and at minor time intervals it is found in the state of transitions between neighboring local minima.

Within the framework of the two-state approach, we restrict the analysis to favorable local minima of the potential energy surface only where the probability to find a cluster is sufficiently high, and ignore locations in intermediate regions of the coordinate space which connect these local minima. The sum of favorable local minima forms the state of aggregation.

Restricting ourselves to one global minimum of the potential energy surface, which corresponds to the ground or solid cluster state, we extract in this way cluster configuration excitations which correspond to the liquid state as favorable local minima of the potential energy surface. In this consideration, only a small interval of time the cluster is found outside the global (as well as close to it) and liquid local minima. In addition, liquid local minima are characterized by nearly equal excitation energies. This way, we have developed a general method of cluster analysis within the framework of dynamics of local minima and saddle points of the potential energy landscape [3, 5, 16]. Note that these considerations refer strictly to zero temperature of systems of bound atoms, only.

15.3 States of Aggregation of a Cluster of 13 Atoms

Defining the aggregate cluster or bulk state as a group of configurationally excited states of the system of bound atoms with nearby excitation energies and a high total statistical weight with respect to the ground state, we below demonstrate the procedure on the example of the simplest cluster which consists of 13 atoms and is bonded by a pair interaction between atoms. This cluster has a icosahedral structure [17] in the ground state (see Fig. 15.1, [18]). The surface of the cluster contains 20 regular triangles formed by joining neighboring surface atoms.

The lowest configurationally excited states of this cluster result from transition of one surface atom on the cluster surface, so that finally this atom is located above the center of a triangle formed by three nearest surface atoms. One can see that there are 15 such atom positions, and because each of 12 surface atoms
can be excited, the total statistical weight of this configurationally excited state at zero temperature is

\[ g = 12 \cdot 15 = 180. \]  \hspace{1cm} (15.4)

One more peculiarity of this excited state is that in the course of transition from the icosahedron vertex to the cluster surface, the transferred atom can conserve only two bonds with surface atoms. Hence, an excited state is separated from other stable atom configurations in the cluster by a barrier, and in order to transfer from this excited state, it is necessary to overcome a barrier whose height is about the energy of breaking of one bond. Fig. 15.2 [19] gives the positions of the levels of these excited states and positions of barriers for transition in these states at zero temperature for the case of a Lennard-Jones pair interaction potential between atoms.

Thus, this example confirms the general character of the behavior of the cluster potential energy which has many local minima separated by barriers. In this case for the lowest excited state we obtain 180 local minima. If we account for other excited states, the number of local minima becomes 988 according to [6]. A more accurate analysis [2] shows the existence of 1488 local minima and 17357 saddle points for the potential energy of this cluster in the case of the Lennard-Jones interaction potential between atoms. Note that in this case we have three
Fig. 15.2 The lowest excited states of a Lennard-Jones cluster of 13 atoms, and the character of their formation through saddle points [19]. Values near levels indicate the excitation energies expressed in units of the binding energy $D$ per one bond. The energies of the close-packed structures are taken from [6]. The lowest excited cluster states may be linked to the cluster's liquid state in which the clusters spend most of the time if they begin with sufficient excitation energy or temperature [20, 21, 22, 23]

degenerated configurationally excited states of this cluster depending on the final distance of a transferred atom from its initial state.

A new property of the phase transition in clusters compared to bulk systems is the coexistence of solid and liquid phases [20 - 26]. This property is shown in Fig. 15.3 where the distribution is given of the total kinetic energies of atoms of a Lennard-Jones cluster which consists of 13 atoms and has the completed icosahedral structure [17], as it is shown in Fig. 15.1 [18]. An excited liquid state is formed as a result of an atom transition from the completed shell to the cluster surface. Coexistence of phases means that a certain part of time the cluster is found in the solid state, and the other part of time it is found in the liquid state.

We now analyze a phase transition that occurs when this cluster is heated. According to the computer simulations [20 - 23], the temperature range of phase
Fig. 15.3 The distribution function of the total kinetic energy of atoms for a Lennard-Jones cluster consisting of 13 atoms. A range near the left maximum corresponds to the liquid state, and the right maximum, with a range close to it, refers to the solid state [22]. $E$ is the total binding energy of atoms, $E_{kin}$ is the total kinetic energy of atoms.

Coexistence for the Lennard-Jones cluster of 13 atoms is $0.29 - 0.31D$, where $D$ is the depth of the Lennard-Jones well, and we take the temperature of the phase transition to be $T_m = 0.30D$. The excitation energy of the liquid state is $\Delta \varepsilon \approx 2.5D$ on average, so that the statistical weight of the liquid state at the melting point with respect to the solid state of this cluster is approximately $g_{liq} = \exp(\Delta \varepsilon / T_m) \approx 4 \cdot 10^3$. The parameters of this phase transition at zero temperature and at the melting point are given in Table 15.1.

We now represent the entropy of the phase transition in the form

$$\Delta S = \Delta S_{conf} + \Delta S_{term},$$  \hspace{1cm} (15.5)

where $\Delta S_{conf} = 5.2$, so that the entropy part due to thermal motion of atoms is $\Delta S_{term} = 2.9$, i.e. it is approximately 35% of the total entropy of this state of aggregation. This part of the entropy is found since the range of motion for an excited atom is wider than that for surface atoms of the icosahedron. Hence, the
reason of this effect is a decrease of the frequency of oscillations for a transferring atom. Taking the limit $T_m \gg h\omega$, where $\omega$ is a typical frequency of atomic oscillations in a cluster, we find that the typical frequency of oscillations of a transferred atom decreases approximately by 3 times. Despite of the roughness of this estimate, it exhibits the nature of the effect of the entropy increase with cluster heating.

15.4 Parameters of Voids for Liquid Rare Gases

Phase transitions in clusters are more complex than in bulk systems, and caloric curves, the temperature dependencies of the current cluster internal energies, allow one to extract several types of phase transitions related to melting of different cluster shells (for example, [26]). As the number of cluster atoms increases, and the cluster is transformed into a bulk system, two types of the phase transition remain, so that the first one relates to internal atoms, and the second one includes surface atoms. In considering melting of bulk systems, we concentrate on the phase transition involving internal atoms, i.e. configurationally excited states of this system result from formation of internal voids [1], and below we use this concept and determine the parameters of these voids.

Being guided by condensed rare gases, we use the connection between a pair interaction of nearest atoms and the total energy of a condensed system of bound atoms. Indeed, one can use the similarity laws by expressing various parameters of different rare gases through the parameters of the pair interaction potential of atoms [14, 27]. In this way, one can express various parameters of different rare gases through three parameters: $m$, the atomic mass, $R_e$, the equilibrium distance between atoms in the diatomic molecule, and $D$, the depth of the potential well for the pair interaction potential of atoms. Analyzing condensed rare gases in these terms, we found that this is a system where interaction between nearest
neighbors dominates [14]. In this case the sublimation energy of the crystal is close to $6D$, because each internal atom has 12 nearest neighbors, and each bond refers to two atoms. In reality, this value is, according to the data given in Table 15.1 [14, 15, 27] $6.5 \pm 0.3$. Next, the reduced pressure near the triple point is [15, 27] $(1.9 \pm 0.2) \cdot 10^{-3}$. Below we ignore the pressure effects. Hence, one can characterize excitation of this system by its entropy.

Thus, considering the configuration excitation of a bulk system of bound atoms with a pair interaction as a result of formation of internal voids, we define a number of internal voids of such a system as a number of initially formed vacancies in a solid which is taken for preparation of this configurationally excited state [15, 30, 31]. A number of voids characterizes a degree of configurational excitation of this system which is not found in equilibrium thermal motion of atoms. In order to prepare a system of bound atoms, consisting of $n$ atoms and $v$ voids, we take a bulk solid cluster of $n + v$ atoms and remove $v$ atoms from the cluster. This system is assumed large enough, so that almost all the removed atoms come from inside the system, and surface effects are negligible. Thus, after relaxation, this system contains $n$ atoms and $v$ internal voids, and according to the definition, an individual void results from relaxation of an individual vacancy and its immediate environment. Because the number of voids can be arbitrary, this system is not at thermodynamic equilibrium and will tend to the equilibrium as a result of diffusion of voids. Therefore we consider this system during short time intervals in comparison with diffusion times of voids through the system. But during this time thermodynamic equilibrium is established with respect to thermal motion of atoms.

Although the volume and shape of an individual void vary in time, we use below average parameters of individual voids which depend only on the void concentration at a given temperature of atomic oscillations. We find the parameters of an individual void in the liquid state near the triple point on the basis of the parameters of real rare gases. Additional information follows from the fact of existence of one thermodynamically stable configuration state of this system, that is the liquid state. Then the logarithm of the partition function $\ln Z = -F/T$, where $F$ is the free energy, as a function of a number of internal vacancies must have the form which is given in Fig. 15.4.

Thus, considering configuration excitations of a system of bound atoms with pair interaction between atoms as a result of formation of some vacancies or voids in this system and neglecting the surface effects for a bulk system of bound atoms, we will find parameters of configuration excitation for the liquid state on the basis of real parameters of rare gases. We assume an elementary configuration excitation
as a void inside the system, and a total excitation is a sum of identical internal voids, so that an individual void is characterized by the statistical weight, \( g_v \), and the average energy, \( \varepsilon_v \), of its formation from the solid state. We make the operations [15, 30, 31] for the determination of these parameters for condensed rare gases, a bulk system of bound atoms with interaction between nearest neighbors only, in a simplified form. This allows us to estimate the accuracy of the model assumptions used.

In considering configuration excitation of a bulk system of \( n \) bound atoms as a gas of \( v \) identical voids, we have for the partition function of voids

\[
Z_v = C_{n+v}^{n} g_v^v \exp \left( -\frac{\varepsilon_v}{T} \right).
\]  

(15.6)

In the bulk limit \( n \gg 1, v \gg 1 \) we have

\[
\ln Z_v = n \ln \left( 1 + \frac{v}{n} \right) + v \ln \left( 1 + \frac{n}{v} \right) + v \ln g_v - \frac{v \varepsilon_v}{T} = v \left( \Delta S_v - \frac{\varepsilon_v}{T} \right),
\]  

(15.7)

where

\[
\Delta S_v = \frac{1}{x} \ln (1 + x) + \ln \left( 1 + \frac{x}{1 + x} \right) + \ln g_v, \quad x = \frac{v}{n}.
\]  

(15.8)
It is convenient to change this expression to

\[
\Delta S_v = 1 + \ln \left( \frac{g_v}{x} \right) .
\]  

(15.9)

This change leads to an error smaller 7%, if \( x \leq 1/3 \), that includes the whole range between solid and liquid states. Then we have

\[
\Phi(x) \equiv \frac{1}{n} \ln Z_v = x \left( 1 + \ln \frac{g_v}{x} - \frac{\varepsilon_v}{T} \right) .
\]  

(15.10)

This simplification allows us to follow the used assumptions.

From this relation, we get for the solid (crystal) state (\( v \ll n, g_v = 1, \varepsilon_v = \varepsilon_{sol} \))

\[
\ln Z_v = v \left( 1 + \ln \frac{n}{v} - \frac{\varepsilon_{sol}}{T} \right) 
\]  

(15.11)

and the minimum condition gives for the number of voids (vacancies) in the solid state

\[
\frac{v_{sol}}{n} = \exp \left( -\frac{\varepsilon_{sol}}{T} \right) .
\]  

(15.12)

This concentration of voids equals for rare gases near the triple point [15, 30, 31] (1.9 ± 0.2) \( \cdot 10^{-5} \). Below we neglect the existence of vacancies for the solid state.

In the case of configurationally excited states, the above expression for the partition function of a void gas is analogous to the general expression Eq. (15.7), i.e.,

\[
\ln Z_v = v \left( \Delta S_v - \frac{\varepsilon_v}{T} \right) ,
\]  

(15.13)

where \( \Delta S_v \) is the entropy of an individual void. In considering the liquid state, we use the relation

\[
v\varepsilon_v = n\Delta H_{fus} ,
\]  

(15.14)

where \( \Delta H_{fus} \) is the enthalpy of the phase transition, and the values of the binding energy per individual void are given in Table 15.2.

Since the dependence on the number of voids for the function \( \ln Z_v/v \) has a specific form (see Fig. 15.4) with two maxima (solid and liquid), this gives additional information for the determination of void parameters for the liquid. We give the
values for some void parameters in Table 15.2, where \( \varepsilon_v = \varepsilon_{\text{sol}} - U \) is the energy which is consumed for formation of one void in the liquid state from the initially solid state.

We take the energy of void formation in the form

\[
\varepsilon_v = \varepsilon_0 - U \left( \frac{V}{n} \right), \quad \frac{U(x)}{\varepsilon_0} = \exp \left( -\frac{\alpha}{x} \right) - \exp \left( -\frac{k\alpha}{x} \right), \quad (15.15)
\]

where \( \alpha \) and \( k \) are parameters. We take as \( \varepsilon_0 \) the crystal sublimation energy per atom \( \varepsilon_{\text{sub}} \) near the triple point or the exponent in the Clausius-Clapeyron law \( \varepsilon_{\text{sol}} \). In the latter case the results of Table 15.2 are given in parentheses.

The equation at the melting point for \( \ln Z_v = 0 \) or \( \Phi(x_{liq}) = 0 \), where \( x_{liq} \) refers to the liquid state, has the form

\[
1 + \ln \left( \frac{g(v_{liq})}{x_{liq}} \right) - \frac{\Delta H_{\text{fus}}}{T_m x_{liq}} = 0, \quad \varepsilon_{liq} = \frac{v_{liq}}{n}. \quad (15.16)
\]
and the solution of this equation exists at

\[ g(v_{liq}) > g_{\text{min}} = \exp \left( \frac{\Delta H_{fus}}{T_m} - 1 \right) . \]  

(15.17)

From this equation and the definition of the energy of fusion \( \Delta H_{fus} = \varepsilon(v_{liq})x_{liq} \) it follows

\[ g(v_{liq}) = \frac{\Delta H_{fus}}{\varepsilon_{liq}} \exp \left( \frac{\varepsilon_{liq}}{T_m} - 1 \right) , \]

(15.18)

where \( \varepsilon_{liq} = \varepsilon(v_{liq}) \) is the energy of void formation for the liquid state at the melting point. Because \( g \) is a monotonic function of \( \varepsilon_{liq} \), and \( \varepsilon_{liq} < \varepsilon_o \), we obtain from this

\[ g(v_{liq}) < g_{\text{max}} = \frac{\Delta H_{fus}}{\varepsilon_o} \exp \left( \frac{\varepsilon_o}{T_m} - 1 \right) . \]

(15.19)

Table 15.2 contains the values of \( g_{\text{min}} \) and \( g_{\text{max}} \).

It is of importance that the liquid state, i.e. a configurationally excited and thermodynamically stable state of a bulk system of bound atoms, exists only if the void statistical weight is found in a certain range. In particular, if the statistical weight of a void is equal to the statistical weight of a vacancy in the crystal lattice \( g = 1 \), the liquid state of such a system is absent. Because the void statistical weight increases with an increase of the temperature of atomic oscillations, thermal motions of atoms are of importance for existence of the liquid state of a system of bound atoms, and this aggregate state is not realized at low temperatures.

Note that at the melting point we have simultaneously

\[ \Phi(x_{liq}) = \Phi'(x_{liq}) = 0 . \]

(15.20)

Taking

\[ g_v = 1 + a \frac{v}{n} , \]

(15.21)

we obtain from Eq. (15.20) at the melting point

\[ \frac{dU(x_{liq})}{dx} = 0 , \]

(15.22)
or
\[ \frac{\alpha}{x_{\text{liq}}} \frac{\ln k}{k - 1} \quad (15.23) \]
and we assume \( g(v_{\text{liq}}) \gg 1 \).

Note that according to its physical nature, the function \( U(v/n) \) is monotonic, and from Eq. (15.22) it follows that the model under consideration is valid only at \( v < v_{\text{liq}} \).

One more equation we obtain, assuming that the minimum of the function \( \ln Z_v \) (see Fig. 15.4) refers to the void concentration when a test void gets a nearest-neighbor void. This gives \( x_{\text{min}} = 1/12 \). Neglecting at this point the second term in Eq. (15.15) for \( U(x) \), and assuming \( g(x_{\text{min}}) \gg 1 \), or \( a \gg 12 \), we obtain from Eq. (15.20) \( \Phi'(x_{\text{min}}) = 0 \)

\[ (1 + 12\alpha) \exp(-12\alpha) = 1 - \frac{(1 + \ln a)T_m}{\varepsilon_0} \quad (15.24) \]

The corresponding values of these parameters are given in Table 15.2.

Of course, these values are close to those of [15, 30, 31], and a difference between them is due to a simplified scheme used now. In spite of the roughness of the used model, it allows us to determine void parameters on the basis of the physical nature of the configurationally excited states.

We now analyze the results from another point of view. We represent the entropy of the phase transition solid-liquid as the sum of two parts

\[ \Delta S = \Delta S_{\text{conf}} + \Delta S_{\text{term}} \quad (15.25) \]

so that the first configuration term is connected with formation of internal voids, and the second term relates to thermal motion of atoms. The first term is equal to

\[ \Delta S_{\text{conf}} = n \ln \left(1 + \frac{v}{n}\right) + v \ln \left(1 + \frac{n}{v}\right) \quad (15.26) \]

and \( \Delta S_{\text{conf}}/n = 0.73 \) for above values of void parameters for condensed rare gases.
15.4 Parameters of Voids for Liquid Rare Gases

Because the total entropy jump for the phase transition of rare gases is \( \Delta S/n = 1.68 \), we obtain for the part due to phonons

\[
\frac{\Delta S_{\text{term}}}{n} = 0.95.
\]  

(15.27)

The nature of this term is connected with oscillations of atoms, and this term represents 56% of the total entropy. As a result of the phase transition, the specific volume per atom increases, as well as the space volume accessible for this atom. This leads to an entropy increase due to atomic motion. If we consider motion of atoms in terms of harmonic oscillations, this effect leads to a decrease of the Debye temperature of this system.

Let us assume for simplicity that the melting point exceeds the Debye temperature \( \theta_D \), so that we use the limiting expression for the entropy of a bulk system of \( n \) bound atoms [28]

\[
S_{\text{osc}} = 3n \ln \frac{T}{\theta_D} + 4n.
\]  

(15.28)

In this limit, taking \( \Delta S_{\text{term}} = S_{\text{osc}} \), we find an increase of the Debye temperature as a result of the phase transition by about 46%. Comparing the contribution from thermal oscillations of atoms to the total entropy of Lennard-Jones cluster

and bulk rare gases at the melting point, one can see that this contribution grows with an increase of the reduced temperature. Indeed, if the reduced melting point \( T_m/D \) increases from 0.3 for the Lennard-Jones cluster consisting of 13 atoms to 0.58 for bulk rare gases, the contribution of atom oscillations at the phase transition to the total entropy jump varies from 36% up to 56%.

We now compare the nature of this phase transition with the Lindemann criterion [11] according to which the phase transition proceeds at the temperature, when the amplitude of atomic oscillations reaches a certain value. This criterion was suggested almost a hundred years ago and more or less corresponds to real parameters of the phase transition. One can see that the nature of the phenomenon under consideration differs in principle from that used in the Lindemann criterion. Indeed, we consider the phase transition as a result of configuration excitation of a system of bound atoms, and because the character of thermal motion of atoms is different for the solid and liquid state, it affects the parameters of the phase transition. The Lindemann criterion does not take into account the configuration excitation of the atomic systems in principle, and connects the phase transition with thermal motion of atoms only. One can see that the validity of the Lindemann criterion in reality is not direct and can be explained by the above influence of thermal motion of atoms on the phase transition.
15.5 Peculiarities of Glassy-like States of Bulk Rare Gases

Let us consider the dependence of the free energy of a bulk system of bound atoms on the void concentration which is shown in Fig. 15.4 for the model under consideration. The minimum of the free energy corresponds to the liquid state which is thermodynamically stable or metastable. As it follows from Fig. 15.5, at the freezing temperature this minimum disappears, i.e. the liquid state does not exist at lower temperatures as a thermodynamically stable state.

![Graph showing the dependence of specific free energy on reduced specific volume for Ar](image)

Fig. 15.5 Dependence of the free energy function of bulk argon on the specific volume [32] at the freezing point 51 K (upper curve), at the temperature of 68 K (intermediate curve) and at the triple point 84 K (lower curve).

Note that we simplify the problem, accounting for only the void concentration dependence for the void statistical weight $g_v$, and the used dependence refers to the melting point. Evidently, according to above analysis, this quantity decreases with a temperature decrease, i.e. the account of the temperature dependence for the void statistical weight leads to an increase of the freezing point. Thus, the freezing point exists irrespectively to the model assumptions. Hence, if we take the liquid state of this system and decrease the temperature, below the freezing temperature this system becomes thermodynamically unstable and decays as a result of departure of voids outside. We call this state the glassy-like state.
15.5 Peculiarities of Glassy-like States of Bulk Rare Gases

According to the standard definition [33 - 36], a glassy state is a frozen-in, thermodynamically non-equilibrium state of a condensed system which can be formed sufficiently fast cooling of the system from a fluid state of thermodynamic equilibrium to low temperatures, to attain a persistent state that is not in equilibrium. Peculiarities of such states first were observed and studied for glasses; therefore we will call these states for other systems glassy-like states. We consider from this point of view a bulk system of bound rare gas atoms below freezing point.

A glassy-like state of condensed rare gases can be prepared by two methods [36]. The first method consists of a fast cooling of liquid rare gases; in the second, a glassy-like state may be prepared as a result of deposition of individual atoms on a target at a low temperature [36, 37]. Deposited atoms occupy initial positions in a random array, and since the temperature is low, atoms cannot move from their initial positions sufficiently far to attain a distribution in thermodynamic equilibrium. This amorphous spatial distribution of atoms is a glassy-like state of a bulk system. A transition to the crystalline state is possible if the temperature is raised enough to allow annealing. Of course, parameters of this glassy-like state differ from those of systems obtained by fast cooling of the liquid state.

Now, we compare these states of bulk rare gases.

Comparing these forms of condensed rare gases, we take into account the structure of the liquid and solid states of aggregation that differ because of the presence of voids in the second case. We define an individual void [15, 30, 31] as the result of relaxation of individual vacancies. When a configurationally excited state of a system of bound atoms is formed from a compact solid state of this system, the formation of some number of vacancies, these transform in voids when the system, with its vacancies, relaxes. In this manner one can form the glassy-like states of condensed rare gases.

Let us consider the evolution of the liquid state of rare gases subjected to fast cooling, or transformation of an amorphous state into the crystalline one as a result of heating. Let us take the rate of transition $1/\tau$ in the Arrhenius form as

$$\frac{1}{\tau} = \frac{1}{\tau_0} \exp \left( -\frac{E_a}{T} \right), \quad (15.29)$$

where the temperature $T$ is expressed in energy units. Considering the cooling
process and assuming the rate of temperature variation $dT/dt$ to be constant, we obtain for a typical time $\tau_c$ of the cooling process

$$\frac{1}{\tau_c} = \frac{1}{\Delta T} \left| \frac{dT}{dt} \right| = \frac{E_a}{T^2} \left| \frac{dT}{dt} \right|,$$

(15.30)

where $\Delta T = T^2/E_a$ is the temperature range in which the transition rate varies weakly. From this we conclude that the instantaneous liquid state structure is conserved at temperatures below the melting point if the cooling rate satisfies the relation

$$\left| \frac{dT}{dt} \right| > \frac{T^2_n}{E_a \tau_o} \exp\left(-\frac{E_a}{T}\right).$$

(15.31)

If this criterion holds true, subsequent cooling down to temperatures below the melting point leads to the transition of the system into a glassy-like state.

Let us consider another scenario, when a bulk system of bound atoms is prepared in an amorphous state at a low temperature, and its heating leads to transition into the ordered solid (crystalline) state. Considering the amorphous state to be a glassy-like one, we define the glass temperature $T_g$ by the relation $\tau(T_g) = \tau_c$. Then, from Eqs. (15.29) and (15.30), we have

$$T_g = \frac{E_a}{\ln\left(\frac{T^2_n}{E_a \tau_o (dT/dt)}\right)}.$$  

(15.32)

Eq. (15.32) connects the parameters of processes that are responsible for the glass transition.

We now take into account the nature of transitions involving the aggregate or glassy-like states of a bulk system of bound rare gas atoms as a result of diffusion of voids in this system to its boundary or from it. Then the rate of transition between aggregate states of a bulk rare gas system or the rate of the glass transition in this system is expressed through the diffusion coefficient $D_v$ of voids which is connected with the self-diffusion coefficient of atoms $D_a$ by the relation

$$D_v = \frac{v}{n} D_a.$$  

(15.33)
15.5 Peculiarities of Glassy-like States of Bulk Rare Gases

<table>
<thead>
<tr>
<th></th>
<th>Ne</th>
<th>Ar</th>
<th>Kr</th>
<th>Xe</th>
<th>Average</th>
</tr>
</thead>
<tbody>
<tr>
<td>$D, K [14]$</td>
<td>42</td>
<td>143</td>
<td>200</td>
<td>278</td>
<td></td>
</tr>
<tr>
<td>$E_{sol}, K$</td>
<td>$480 \pm 20$</td>
<td>$1900 \pm 100$</td>
<td>$2500 \pm 100$</td>
<td>$3700 \pm 100$</td>
<td></td>
</tr>
<tr>
<td>$E_{sol}/D$</td>
<td>$11.4 \pm 0.5$</td>
<td>$13.3 \pm 0.7$</td>
<td>$12.5 \pm 0.5$</td>
<td>$13.3 \pm 0.4$</td>
<td>$12.6 \pm 0.9$</td>
</tr>
<tr>
<td>$E_{liq}, K [39, 40]$</td>
<td>113</td>
<td>352</td>
<td>402</td>
<td>607</td>
<td></td>
</tr>
<tr>
<td>$E_{liq}/D$</td>
<td>2.69</td>
<td>2.46</td>
<td>2.01</td>
<td>2.18</td>
<td>2.3 $\pm$ 0.3</td>
</tr>
<tr>
<td>$\epsilon_{liq}/D$</td>
<td>2.1</td>
<td>2.0</td>
<td>2.1</td>
<td>2.1</td>
<td>2.1 $\pm$ 0.1</td>
</tr>
<tr>
<td>$D_o, \text{cm}^2/\text{s}$</td>
<td>0.27</td>
<td>0.37</td>
<td>0.15</td>
<td>0.22</td>
<td></td>
</tr>
<tr>
<td>$l^2[(dT/dt)_{liq}]_m/\text{K} \cdot \text{cm}^2/\text{s}$</td>
<td>0.014</td>
<td>0.11</td>
<td>0.15</td>
<td>0.22</td>
<td></td>
</tr>
</tbody>
</table>

Tab. 15.3 Parameters of void diffusion in condensed rare gases

As an activation process, diffusion of voids is characterized by an activation energy. Note that for the solid state the number of vacancies is

$$v \sim \exp\left(-\frac{\epsilon_v}{T}\right),$$ (15.34)

$\epsilon_v$ being the energy of vacancy formation. Hence the activation energies for the self-diffusion coefficients of atoms $E_a$ (data for this parameter are given in Table 15.3, they are taken from [38]), and the diffusion coefficients of voids-vacancies ($E_{sol}$) differ from those of the solid state by the energy $\epsilon_v$ of formation of an individual vacancy ($E_{sol} = E_a + \epsilon_v$). In the case of the liquid state, for which $v \sim n$, the activation energies for these diffusion processes are identical.

Table 15.3 contains the activation energies for diffusion of voids in the solid ($E_{sol}$) and liquid ($E_{liq}$) states. The diffusion coefficient of voids for the liquid state has the form

$$D_v = D_o \exp\left(-\frac{E_{liq}}{T}\right),$$ (15.35)

and the parameters of this formula in Table 15.3 follow from measurements of the self-diffusion coefficients of atoms in liquid rare gases [39, 40] and formula Eq. (15.34).

In addition, in Table 15.3, we compare the energy of formation of an individual void $\epsilon_{liq}$ for the liquid aggregate state near the triple point with the activation energy $E_{liq}$ of the diffusion process for voids in the liquid and find that these values are identical with a reasonable accuracy. Hence, one can assume equality.
of the activation energy $E_a$ for diffusion of voids in Eq. (15.29) and the energy of formation $\varepsilon_v$ of a new void.

Note that the quantity $\varepsilon_{liq}$ of Table 15.3 differs from the quantity $\varepsilon(v_{liq})$ of Table 15.2. Indeed, $\varepsilon(v_{liq})$ is the average energy of void formation, if we start from the crystal state. This value is equal to $\varepsilon_0 - U(v/n)$, where $\varepsilon_0$ is the energy for atom removal from the crystal lattice, and $U(v/n)$ is the effective energy of void interactions. It is the energy released per void as a result of shrinkage of this system after removal of $v$ atoms, if this system contains $n + v$ atoms at the beginning. In contrast to this quantity, $\varepsilon_{liq}$ is the energy of formation of a new void if the system is found in the liquid state. Within the framework of the model under consideration, the latter is equal approximately to

$$\varepsilon_{liq} = \varepsilon(v_{liq}) - \Delta H_{fus}. \quad (15.36)$$

Considering diffusion of voids, we take a condensed rare gas, for simplicity, in the form of a plane film of thickness $l$ located on a target. Then a typical diffusion time is equal to

$$\tau = \frac{l^2}{D_v}. \quad (15.37)$$

In this case, Eqs. (15.31), (15.34) and (15.37) give the cooling rate for formation of a glassy-like state of a film as a result of fast cooling in the form

$$\left| \frac{dT}{dt} \right| > \left| \left( \frac{dT}{dt} \right)_{lim} \right| = \frac{T_m^2}{E_{liq}l^2} D_v \exp \left( -\frac{E_{liq}}{T_m} \right). \quad (15.38)$$

Table 15.3 gives the threshold values of the parameter $l^2 |dT/dt|$ which assures formation of glassy-like states of rare gases as a result of cooling of liquid rare gases.

### 15.6 Glass Transition at Heating

One can use various parameters of the system in order to distinguish the solid and glassy-like states; for this purpose, we will use the saturated vapor pressure over
15.6 Glass Transition at Heating

A planar surface of the system, being guided by the experiment [37]. According to the Clausius-Clapeyron law, the saturated vapor pressure is given by [28, 41]

\[ p(v, T) = p_o \exp \left( -\frac{\varepsilon(v)}{T} \right) \]  \hspace{1cm} (15.39)

where \( \varepsilon(v) \) is the mean binding energy of a surface atom, which is the sublimation energy per atom for a bulk system with a given number of voids \( v \) inside it. We assume that the saturated vapor pressures, referred to any concentration of voids, are identical at the triple point, as it is the case for the solid and liquid states. This gives for the pre-exponential coefficient

\[ p_v = p_o \exp \left( \frac{\varepsilon(0) - \varepsilon_{sol}}{T_{tr}} \right) \]  \hspace{1cm} (15.40)

where \( \varepsilon_{sol} \) is the binding energy per atom for the solid state, and \( \varepsilon_{sol} = \varepsilon(0) \), \( p_o \) is the pre-exponential factor in Eq. (15.40) for the solid state, and \( T_{tr} \) is the triple point temperature. It follows from this formula that the pre-exponential factor in Eq. (15.39) drops as the density of voids increases. Of course Eq. (15.40) is correct for the liquid state.

From this we have

\[ \frac{p(v, T)}{p_{sol}(T)} = \exp \left[ (\varepsilon_{sol} - \varepsilon(v)) \left( \frac{1}{T} - \frac{1}{T_{tr}} \right) \right] \]  \hspace{1cm} (15.41)

where \( p_{sol}(T) \) is the saturated vapor pressure over the solid surface at a given temperature. In particular, for the metastable liquid state at a temperature \( T \) below the triple point, Eq. (15.41) gives

\[ \frac{p_{liq}(T)}{p_{sol}(T)} = \exp \left[ \Delta H_{fus} \left( \frac{1}{T} - \frac{1}{T_{tr}} \right) \right] \]  \hspace{1cm} (15.42)

\( \Delta H_{fus} \) is the specific enthalpy of fusion.

Along with the temperature of the glass transition, which is given by formula Eq. (15.32) and characterizes the equality of the rate of heating and the process of void diffusion, we introduce the temperature \( T_g \), from which the subsequent growth of the saturated vapor pressure can proceed. For heating of an amorphous state of a rare gas this temperature is defined according to the relation

\[ p(v, T_g) = p_{sol}(T_*) \]  \hspace{1cm} (15.43)
and according to formula Eq. (15.41) we have

$$\varepsilon(v) \left( \frac{1}{T_g} - \frac{1}{T_{tr}} \right) = \varepsilon_{sol} \left( \frac{1}{T_r} - \frac{1}{T_{tr}} \right).$$  (15.44)

![Diagram](image)

**Fig. 15.6** Temperature dependence of the saturated vapor pressure above heated amorphous argon formed by deposition of the argon flux on a copper substrate at the temperature 10 K [37] and its approximation in limiting cases [36] referred to the glassy-like (fluid) and crystal argon states.

Let us use, now, these formulas to analyze the results of the experiment [37] (see Fig. 15.6) in which amorphous argon was prepared by deposition of an argon vapor on a copper substrate at a temperature of 10 K; the triple point of bulk argon is $T_{tr} = 83.7$ K. Warming leads to an annealing transition to the crystal state [36, 37]. A typical film thickness in this experiment is 10μm, exceeding the distance
between nearest neighbors of bulk condensed argon by more than three orders of magnitude. Hence this film can be considered as bulk condensed argon. A rate of heating $dT/dt \approx 2K/min$ leads to the glass transition at $T_g = 20 \pm 1K$, and the saturated vapor pressure starts to grow from the temperature $T_s = 24 \pm 1K$.

The results of this experiment are compared with the above formulas in Table 15.4 if we assume the amorphous state to be structurally analogous to the liquid state and treat experimental data on the basis of Eqs. (15.32) and (15.44). This comparison shows the identity of the amorphous state of argon obtained by deposition of atoms on a cold target and the glassy-like state that we have described as a frozen-in liquid state at low temperatures.

<table>
<thead>
<tr>
<th>Experiment [37]</th>
<th>$T_g, K$</th>
<th>$T_s, K$</th>
<th>$\varepsilon(v), K$</th>
<th>$E_a, K$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Theory for liquid</td>
<td>$20 \pm 1$</td>
<td>$24 \pm 1$</td>
<td>$730 \pm 90$</td>
<td>$330 \pm 20$</td>
</tr>
</tbody>
</table>

Tab. 15.4

From this analysis for simplest bulk systems of bound atoms and clusters it follows that glass and phase transitions have a common feature which consists in a change of configurational excitation in such transitions. The difference between these phenomena is such that thermal excitation of bound atoms influences the phase transition, in particular. For glassy-like states of a system of bound atoms thermal motion of atoms is not so important. Kinetics of voids determines the decay of glassy-like states.

We note also the example of a solid-solid phase transition in a large cluster [42, 43] in which the vibrational contribution to the thermodynamic parameters in this phase transition is quite small. This phase transition gives a small contribution to the thermodynamic parameters of clusters, in contrast to the solid-liquid phase transition.

Thus, the void concept describes simultaneously both formation of the liquid states and glassy-like states. These voids are formed inside bulk systems or on the surface of not too large clusters. Thermal vibrations of atoms influence significantly the entropy of configuration excitation states at the melting point, and are not of importance for the glassy-like states, since they exist at low temperatures where this influence is weak.
15.7 Conclusions

Considering clusters bound by pair interactions between atoms, we assume these atoms can be treated as classical and examine two types of excitations, configurational excitations and phonons. Phonons result from vibrational motion of atoms, whereas a configuration excitation leads to a change of the atomic configuration. Both the true solid-liquid phase transition and the glassy transition result primarily from transitions involving configurationally excited states of the cluster. Parameters of bulk condensed rare gases and computer modeling of clusters allow us to understand these phenomena in detail. Assuming voids to be elementary configurational excitations in this system, one can find the void parameters by employing the results of computer simulations of clusters and the parameters of the liquid state of rare gases at the melting point.

In the case of not too large clusters, systems exhibiting a finite number of locally-stable configurationally-excited states formed by transition of atoms from completed cluster shells to the surface conform to the above model of the liquid and glassy-like states which result from formation of surface voids. Annihilation of voids results in a transition of atoms from the cluster surface to the outermost shell. This glassy-like state may be considered also from the point of view of the concept of cluster configurational excitation as a result of transition to local minima of the potential energy surface of this cluster. Because neighboring local minima of the cluster's configurational energy are separated by barriers, transitions from the ground cluster shell to excited configurations have an activation character. Thus, the void concept of the liquid and glassy-like states can be combined with our knowledge of evolution of clusters as transitions between local minima of the potential energy surface of clusters. The combination of these concepts is of importance for a more detailed understanding of the cluster behavior.

Focusing on simple systems of bound atoms, such as condensed rare gases and cluster bonded by pair interactions, we show the nature of configuration excitation of these systems as a result of formation of voids, and the void concept can be combined with the concept of the potential energy landscape for clusters and classical thermodynamics. In addition, the void concept exhibits that though the Lindemann criterion for the phase transition has a not correct basis, it gives the true tendency in the influence of thermal oscillations of atoms on the phase transition in clusters and bulk systems through parameters of configurationally excited states.

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