

THE CONNECTION BETWEEN COEFFICIENT CLUSTERISATION WITH TEMPERATURE

Mast. of Phys. Liaushuk I.¹, Assoc. Prof. Dr. Eng. Auchynnikau Y.², Assoc. Prof. cand. Eng. Nikitin A.³, Prof. Dr. Phys. and Math. Liopo V.⁴

Faculty of Physics and Technology^{1,3,4} – Yanka Kupala State University of Grodno, Belarus,

E-mail: ilavshuk@grsu.by, : nik@grsu.by, liopo@grsu.by

Faculty of Innovative Technologies of Mechanical Engineering² – Yanka Kupala State University of Grodno, Belarus,

E-mail: ovchin@grsu.by

Abstract: A statistical model is proposed to analyze the relationship between the clustering coefficient (CC) and the temperature and atom-atom interaction potential. CC is defined as the ratio of the number of atoms in clusters to the total number of atoms in a system. The proposed technique is based on the statistical concept of entropy. The clustering coefficient is considered for the equilibrium state.

KEYWORDS: CLUSTERED LIQUID, CLUSTERING, FREE ENERGY, INTERATOMIC POTENTIAL, ENTROPY.

1. Introduction

$$a_n / n \equiv a \quad (1)$$

In various liquids there are regions with a large number of atoms with degree of ordering more than the average for the whole volume of the liquid. Such regions are called as clusters, and the fluids in which they emerge are called as clustered. At a temperature close to the evaporation one temperature, the concentration of clusters is minimal, and at crystallization their concentration has maximal value. If the number of atoms in the system is N and the number of atoms in the clusters is C , the ratio $q = C / N$ is a clustering coefficient (CC). Each cluster is a dynamic system with a lifetime τ . But the total number of atoms C remains unchanged if $T = \text{const}$. The value q at a fixed temperature depends on the properties of the liquid, which are individual for each liquid substance. It means that cluster have possibility to appear and to disappear. But the dependence $q = q(T)$ has common form.

This fact may be explained on the basis of methods of physical kinetics.

The aim of the research is to create a mathematical model based on the minimization of free energy at the equilibrium state of the cluster system.

The object of the investigation is the Helmholtz equation, which includes the potential of atom-atom interaction and entropy of the system.

The object of the research is the relationship between CC, temperature and potential of atom-atom interaction.

There are following research tasks:

1. To construct a model for calculating the entropy of a cluster system at a fixed free energy when $T = \text{const}$;
2. To look for a connection between the CC and the internal energy for isothermal conditions at equilibrium;
3. To show that the CC in liquids monotonically decreases if temperature changes from the melting point of the crystal (T_{cr}) to the point of evaporation of the liquid (T_{ev}).

2. Degree of atomic-molecular ordering

Crystalline objects are atomic-molecular systems with regular arrangement of homologous points in any direction. This means that if one selects any point in the crystal and draw a straight line through it, then on this straight line, at a distance from the initial point equal to a , there's a point absolutely identical in structural and chemical relation to the starting point. For an ideal crystal, the distance from the initial point to n -th point (a_n) is described by the condition:

In real crystals, the distance from the starting point to the n -th one equals to:

$$a_n / a = n + \Delta \quad (2)$$

This is explained by the fact that the distances between neighboring atoms fluctuate. As repulsive forces are significantly stronger than attractive forces at the same change $a_n - a_{n-1}$, then Δ in formula (2) is always positive. If the Δ exceeds any fixed value, for example $a/2$, the value of n determines the degree of ordering. For perfect crystals $n \Rightarrow \infty$, for gases $n=1$.

The degree of ordering is a subjective characteristic to some extent, since Δ can take other values. For example, if Δ_1 is accepted as equal to $a/2$ or $\Delta_2 = \frac{a}{4}$, that the degree of ordering in the first case "will appear" higher.

However if the same limit value is taken for a number of samples with the same structure and composition but different concentrations of defects, then regardless of its magnitude a hierarchical series is constructed from the sample with the highest degree of ordering to the sample with a lower value q or vice versa.

If the substance in the crystalline state is described by the $Fm\bar{3}m$ group, which corresponds to a three-layer closed sphere package, for an ideal crystal, the radius of the n -th coordination sphere is equal to:

$$R_n = \sqrt{n} \cdot d, \quad (3)$$

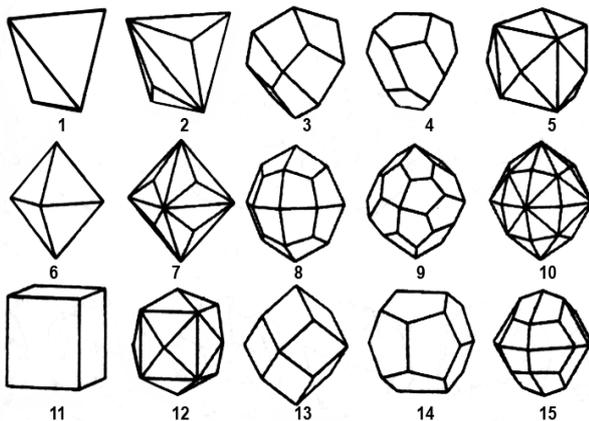
where d is the diameter of the atom.

That is, a monoatomic substance is considered, in which, within the framework of the model of the densest sphere packing, the degree of ordering determines the defect of the crystal due to various factors.

The example of these objects is metallic crystals [1]. In this case, the criterion of the degree of ordering is the difference of the radius of the n -th coordination sphere and its number for metals of the corresponding point $Fm\bar{3}m$ group or other groups. In particular for metals with $Fm\bar{3}m$, $Im\bar{3}m$, $6/mmm$ point groups. These three groups describe the structures of almost all metals, ice and other substances.

In liquid environment, the average atom-atom distance is almost equal to the value for crystalline objects. But the degree of atomic ordering in liquids is much lower than in crystals. So for liquids the notion of middle and even closest order applies. At the same time, groups of atoms can interact with each other to create a three-dimensional configuration similar to a nanocrystalline particle.

As the temperature decreases, the stability of this system increases. At the point of crystallization, each system of this kind which is called a cluster, becomes the center of crystallization. That is why metals create polycrystalline objects during crystallization. Let's consider the correct forms of crystals of the $Fm\bar{3}m$ group.



1. Tetrahedron
2. Trigontrioctahedron
3. Tetragontritetrahedron
4. Pentagontritetrahedron
5. Hexatetrahedron
6. Octahedron
7. Trigotrioctahedron
8. Tetragontrioctahedron
9. Pentagontrioctahedron
10. Hexaoctahedron
11. Hexahedron
12. Tetrahexahedron
13. Rhombododecahedron
14. Dodecahedron
15. Didodecahedron

Fig. 1. - The cubic crystals polyhedral right forms

Figure 1 shows the names of possible polyhedra.

These habits are preserved for the nanocrystals. As the particle size increases, the polyhedral form takes the shape of a sphere, as the $Fm\bar{3}m$ group in the limiting transition from a polyhedron to a sphere becomes a group of infinite order $\infty : \infty \cdot \infty$.

In general case, clusters are the objects with the following characteristics. The first, the degree of atomic ordering is greater than the average volume of the cluster fluid; secondly, they are a dynamic system, which even in thermostatic conditions disappear and occur in other parts of the system.

The total number of atoms in the cluster state remains unchanged.



Fig. 2. – Macroscopic model of the atomic cluster

An example of a cluster system is shown in figure 3, which demonstrates that clusters with structural characteristics different from non-clustered matrix are visible in the electron-microscopic image of the pure metal.

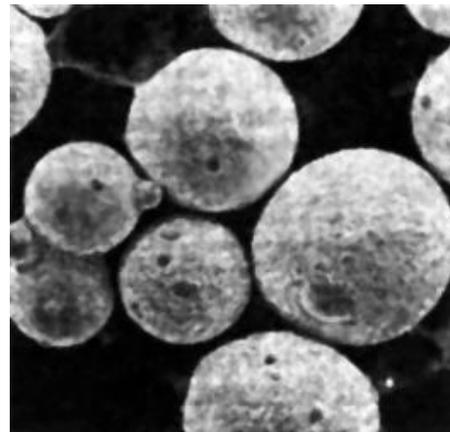


Fig. 3. – Electron microscopic image of copper particles, magnification $5.2 \cdot 10^{-7} m$ [2].

3. The Helmholtz equation for cluster liquids

To determine the relationship of the clustering coefficient for liquids, the Helmholtz equation was used which is applicable for solids, liquids and gases, especially for cases with high pressure.

This equation has the form:

$$F = U - TS, \tag{4}$$

where F is the free energy of Helmholtz or the isochoric-isothermal thermodynamic potential determined by the difference between the total energy and the parameter configuration, depending on the number of States in thermodynamic equilibrium.

The total energy U is the sum of the kinetic energy of the motion of atoms (ions, molecules) and potential energy of atom-atom interaction. The kinetic energy of one atom modeled by a sphere with three degrees of freedom is:

$$K = 3kT, \tag{5}$$

where k is Boltzmann's constant.

For polyatomic molecules

$$K = f kT, \tag{6}$$

where f is a factor depending on the number of degrees of freedom of an atom (ion, molecule).

The potential energy of the pair atom-atom interaction (P) in the general case can be represented as:

$$P = \alpha \exp \frac{E}{kT}, \tag{7}$$

When α, E are energetical parameters which depends on properties of matter and start temperature point.

If is consider the following temperature range:

$$T_{cr} < T < T_{ev}, \tag{8}$$

where T_{cr}, T_{ev} – crystallization and evaporation temperatures respectively.

For specific situations, the form of the potential may be different [3]. The potentials of Lennard – Jones, Morse, of Sutherland, Yukawa, models of hard spheres, quantum wells with different parameters [4, 5]. All these potentials can be considered as constants for fixed interatomic distances. If the temperature increases, the atom-atom distance increases. This means that the parameter of atom-atom interaction decreases with increasing temperature. That is, this degree of approximation is applicable to the analyzed temperature range.

Entropy $S = k \ln \Omega$, where Ω is the number of the system states. In this case entropy as thermodynamic function has statistical sense. General number of atoms (ions, molecules) equal N in the system. From N atoms C atoms are displaced in clusters. That is,

$$C/N = q, \quad (9)$$

it is a clustering coefficient with $0 \leq q \leq 1$.

Atoms in a cluster interact with each other.

The total potential energy for all clusters is equal to

$$U_c = \frac{C}{2} \alpha \exp \frac{E}{kT}, \quad (10)$$

For atoms outside the cluster system, the gas model is applicable, when atoms interact only in a collision.

This model is used not only for liquids but also for solids [6]. On its basis it is proved that

$$C_V(T)_{T > \theta_D} = 3R, \quad (11)$$

where θ_D – Debye temperature.

This conclusion is in good agreement with the experiment, which indicates that classical concepts are applied legitimately.

The total energy in the Helmholtz equation (4) for the system under consideration is

$$U(T, C) = (N - C)fkT + \frac{C}{2} \alpha \exp \frac{E}{kT}, \quad (12)$$

The scheme of change of the clustering coefficient for any cluster systems is shown in figure 4.

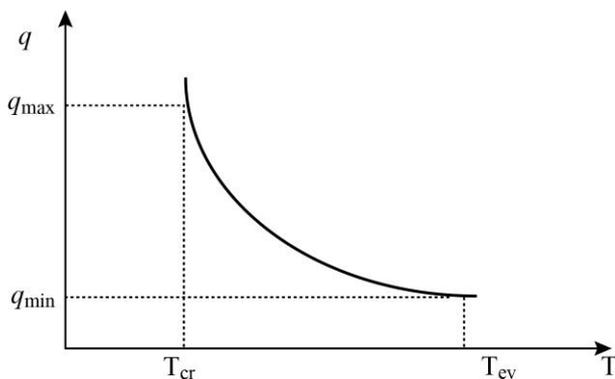


Fig. 4 – The scheme relation between coefficient of clusterization (q) and the temperature (T) [2].

From this scheme clearly visible, that q_{\max} meets the requirements T_{cr} , and $q_{\min} - T_{ev}$.

The numerical values of these parameters depend on the properties of the substance and the methods of temperature change. For example, the sudden cooling of the melt (method of

spinningovye or punching through the capillary) can be fixed clustering for intermediate temperatures of the melt.

4. The entropy of a cluster system

The cluster system can be considered as a two-phase substance with phase concentration $(N-C)/N$, C/N .

In the framework of the classical kinetic model atoms are distinguishable, that is, the number of States in the system (Ω) is determined by the condition:

$$\Omega = \Pi_{(N-C)} \cdot \Pi_C = (N - C)! C!$$

$$S = k \ln \Omega = k \cdot \ln(N - C)! + \ln C!, \quad (13)$$

When $\Pi_{(N-C)}$ is according to Stirling's formula and ($X \gg 1$)

$$\ln X! = X \ln X - 1 = X \ln X, \quad (14)$$

and considering that N , $N-C$, C immeasurably more than one, we get:

$$S = k \ln \Omega = k((N - C) \ln(N - C) + C \ln C) = k[N(1 - q) \ln N(1 - q) + qN \ln qN] \quad (15)$$

According to formulas (13 – 15) the Helmholtz equation (4) will take the form:

$$F(T, q) = N(1 - q)fkT + q \frac{N}{2} \alpha \exp \frac{E}{kT} - kT \{ N(1 - q) \ln N(1 - q) + q \cdot N \ln qN \} \quad (16)$$

Free energy at a constant temperature depends only on the degree of clustering determined by the value of the clustering coefficient q . When the system is in the equilibrium state the following ratio must be true

$$\frac{dF}{dq} = 0. \text{ Then}$$

$$\frac{1 - q}{q} = \left(0,5 \exp \frac{E_0}{kT} - fkT \right). \text{ Then}$$

$$F(q) = (1 - q)fkT + \frac{q}{2} \cdot \alpha \exp \frac{E}{kT} + (1 - q) \ln N(1 - q) + q \cdot \ln Nq \quad (17)$$

At a constant temperature, the equilibrium state of the system is determined by condition:

$$\frac{dF}{dq} = 0. (T = \text{const}).$$

That is:

$$\left(-fkT + \frac{1}{2} \alpha \exp \frac{E}{kT} + kT \ln \frac{q}{(1 - q)} \right) = 0, \quad (18)$$

From here

$$\ln \frac{q}{1-q} = \frac{\alpha}{2kT} \cdot \exp \frac{E}{kT} - f, \quad (19)$$

In thermostatic conditions, the clustering coefficient of the system depends on only the potential of atom-atom interaction.

In the quasi-stationary transition to higher temperatures, the right side of the equation (19) decreases, hence the clustering coefficient also decreases. Using the model the size of clusters and their shape cannot be determined. Because it needs property of matter.

However, given the dynamic processes of cluster formation, we can understand why, for example, it is very difficult to obtain single crystals during solidification of cluster fluids.

Each cluster at a lower temperature is characterized by a longer lifespan and can become the embryo of the crystal.

At sharp cooling of metal melts, when relaxation in the cluster is not achieved, the metal solidifies.

Since the cluster does not necessarily reflect the symmetry of the crystal state, structures can occur even with non-crystallographic symmetry.

This may explain the example of quasi-crystalline objects with pentagonal symmetry.

5. Conclusion

The model of calculation of entropy of cluster system for conditions of thermostatic equilibrium has been constructed.

The relationship between the clustering coefficient and the internal energy for isothermal conditions at equilibrium has been analyzed.

The focus of the study has been the dependence of energy freedoms on temperature, the parameters of the atom-atom interaction potential and the ratio of the number of atoms in clusters to the total number of atoms in the system, also known as the clustering coefficient.

It is found that the clustering coefficient in liquids monotonically decreases with temperature change from the melting point of the crystal to the point of evaporation of the liquid.

The proposed model for determining the dependence of the clustering coefficient (q) in cluster fluids, based on the method of physical kinetics, explains the dependence of the clustering coefficient (q) on temperature T , and is applicable to all types of atom-atom interaction potentials.

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