

Comparison of Classical Nucleation Theory and Modern Theory of Phase Transition

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Abstract

The formation of electrochemical phase is a typical example of a first-order phase transition. An overview on old and new thermodynamic and kinetic aspects of the theoretical description of first-order phase transitions, and, in particular, of the theory of nucleation is given. Electrochemical nucleation of nanostructures has been considered in terms of the classical Gibbs and the Cahn-Hilliard-Hillert theories. We obtained agreement between the theories Kahn-Hilliard-Hillert and Gibbs.

Keywords: Electrochemistry; Nucleation; Nanoparticles; Phase transitions; Gibbs theory; Cahn-Hilliard theory

Introduction

Electrochemical nucleation is usually described in the framework of the classical Gibbs theory of nucleation, which provides a simple expression for the critical radius of a growing nucleus (nanoparticles) [1-11]:

$$r_c = K(\gamma/\mu) \quad (1)$$

where γ is the specific surface energy, μ is the change in volume energy during a phase transition (e.g., nucleation), and K is the particle shape factor.

The electrochemical kinetic reactions are determined by the magnitude of energy barrier ΔE_c (activation energy) [5-9], which can be controlled by the surface energy, volume energy and shape factor. The steady flow rate of formation of the most probable nuclei can be defined as follows [3-9]:

$$J \sim \exp \{-\Delta E_c / k_b T\} \quad (2)$$

where k_b is the Boltzmann constant, and T is the absolute temperature.

The dimensionless parameter G , which is also referred to as the Gibbs number, describes, equilibrium electrochemical nucleation and has the form [5]:

$$G = \Delta E_c / kT \quad (3)$$

Further, we briefly describe essential points of calculate ΔE_c adopted in the classical Gibbs model first and then address modern theory of phase transitions.

Classical Gibbs Nucleation Theory

Energy ΔE_c in the classical Gibbs nucleation theory (for a three-dimensional case) was obtained by assuming that the nucleus is a sphere of radius r [1-9]:

$$G_3 = G_{3p} - G_{3v} = 4\pi r^2 \gamma_3 - (4/3)\pi r^3 \mu_3 \quad (4)$$

where γ_3 is the specific surface energy (for the three-dimensional case), μ_3 is the change in volume energy during a phase transition (for the three-dimensional case).

The size of the critical radius of nucleation r_c is determined in Equation 1 (where for the three-dimensional case: $K_3=2$):

$$r_c = 2\gamma/\mu$$

Critical nucleus radius corresponding to maximum G_3 is as follows (Figure 1) [1-9]:

$$\Delta G_3 = (16\pi/3)(\gamma_3^3 / \mu_3^2) \quad (5)$$

For a two-dimensional case, we obtain [1-9]

$$\Delta G_2 = G_{2p} / 2 = \pi(\gamma_2^2 / \mu_2)$$

where γ_2 is the specific surface energy (for the two-dimensional case), μ_2 is the change in volume energy during a phase transition (for the two-dimensional case).

The size of the critical radius of nucleation r_c is determined in Equation 1 (where for the two-dimensional case: $K_2=1$):

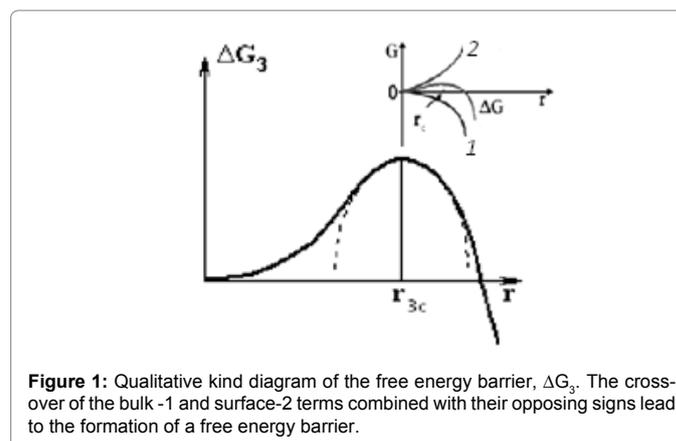


Figure 1: Qualitative kind diagram of the free energy barrier, ΔG_3 . The cross-over of the bulk -1 and surface-2 terms combined with their opposing signs lead to the formation of a free energy barrier.

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$$r_2 = \gamma / \mu$$

Critical nucleus radius corresponding to maximum G_2 is as follows [1-9]

$$\Delta G_2 = G_{2p} / 2 = \pi(\gamma_2^2 / \mu_2) \quad (6)$$

The generalization can be obtained for a multidimensional system:

$$r_{nc} = (n-1)(\gamma_n / \mu_n) \quad (7)$$

And

$$\Delta G_n = G_{np} / n \quad (8)$$

According to Equation 7, in one-dimensional case,

$$r_{1c} = 0 \quad (9)$$

because $K_1 = 0$.

This finding is consistent with the general theory. In terms of the droplet model, for convex surfaces, one can obtain the following expression:

$$k(i) \sim \frac{S'(r)r}{V'(r)} \quad (10)$$

To calculate energy barrier ΔG , it is necessary to know the surface energy and particle shape factor $k(i)$:

$$\Delta G_i \sim G_p / [k(i) + 1] \quad (11)$$

Energy barrier ΔG can be assumed to be proportional to cathode overpotential η_k (see, e.g., [5,10,11]). This dependence can be presented as follows:

$$\Delta G_n \sim 1 / (\mu_n)^{n-1} \sim 1 / (\eta_k)^{n-1} \quad (12)$$

It was experimentally studied for the case of $n=2$ and 3 , which follows from Equations 8-12 (see, e.g., [11]). Other general findings are given below. Here, we note that, if the short-range interaction covers the following focal areas, then radius r_{nc} increases to infinity, while the energy barrier vanishes. It was found that, for spinodal disintegration, the radius (which is similar radius r_{nc}) increases indefinitely, while the energy barrier decreases.

Ginsburg-Landau-Abrikosov Theory and Cahn-Hilliard Theory Applied to Nucleation

The Ginsburg-Landau-Abrikosov theory uses free energy (Hamiltonian) in form [12-15]

$$H(\Sigma) = \alpha (\nabla \Sigma)^2 + A\Sigma^2 + C\Sigma^4 + 13\Delta$$

where order parameter Σ is a generalized spinor (linear term is omitted).

Function $H(\Sigma)$ extreme condition allows deriving a differential equation. This equation was obtained in [14,15]:

$$\theta''(\rho) + ((L-1)/\rho)\theta'(\rho) - F[a, \rho, \cos\{\theta(\rho)\}, \sin\{\theta(\rho)\}] = 0 \quad (14)$$

$$1/\alpha = (\alpha/A)^{1/2}$$

where L determines the space dimensionality of spinor (nD -dimensionality), and $F[a, \rho, \cos\{\theta(\rho)\}, \sin\{\theta(\rho)\}]$ is a polynomial (analytical function) that can be defined in each case.

Application of Equation 14 to a 2D problem was thoroughly considered in [15]. Below, we consider a 1D case ($L=1$), which corresponds to the Cahn-Hilliard-Hillert theory [16-22].

The resulting equation has the form

$$\theta''(\rho) = (a/2)\sin\{2\theta(\rho)\} \quad (15)$$

which is similar to previously reported equations [16-22] and according to which it is possible to obtain the solution [15]:

$$\cos\{\theta(\rho)\} = -\tanh\{a\rho\} \quad (16)$$

The size of the domain wall is an important parameter determining the nucleating seed size (Figure 2):

$$\delta_{LL} = 1/a = (\alpha/A)^{1/2} \quad (17)$$

Assuming that the domain wall size determines the critical radius of a nanoparticle, the difference between Equations 1 and 17 should be noted.

It can be shown that the energy of the domain wall is also different from the classical formulas given by Equations 5 and 8:

$$E_{LL} = (\alpha A)^{1/2} \quad (18)$$

Agreement between the Ginsburg-Landau-Abrikosov (Cahn-Hilliard-Hillert) theories and the classical Gibbs nucleation theory is discussed below.

Unification of the Theories

The simplest assumption regarding the relationship between the surface tension and the nanoparticle radius can be expressed as follows:

$$r_{eff} \approx \gamma / r_{rel} \quad (19)$$

$$\text{and } \left(r_{rel} = r_c / \Delta_{in} \right) > 1$$

where Δ_{in} is the thickness of the surface layer of the nanoparticle and $\left(r_{rel} = r_c / \Delta_{in} \right) > 1$ is a parameter of length characterizing the nanoparticle size in terms of Δ_{in} .

If $r_{rel} < 1$, then the Gibbs theory is not applicable. However, it can be applied in accordance with the Cahn-Hilliard-Hillert theory. In this case, a formula similar to Equation 1 (or Equation 7 without taking into account the k_n factor) can be written as follows:

$$r_c \approx \gamma_{eff} / \mu \approx \Delta_{in} \gamma / r_c \mu \quad (20)$$

It is not difficult to transit to the formulas in the form of Equation

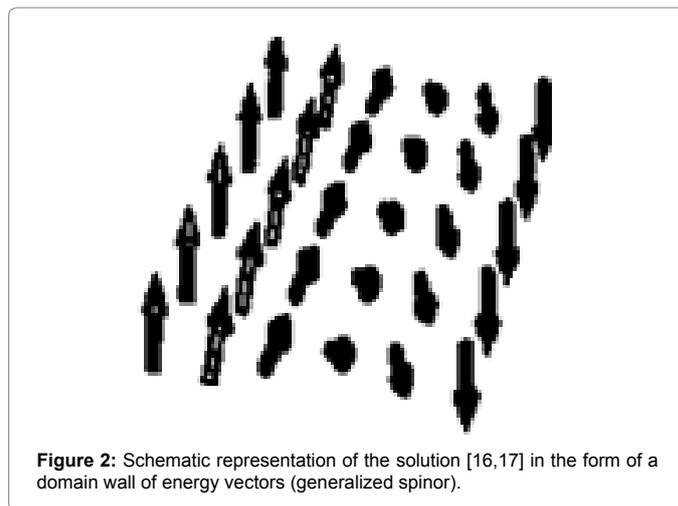


Figure 2: Schematic representation of the solution [16,17] in the form of a domain wall of energy vectors (generalized spinor).

17 from the Cahn–Hilliard–Hillert theory:

$$r_c^{(KXX)} \approx \left(\frac{\Delta_m \gamma}{\mu} \right)^{1/2}, \quad (21)$$

If

$$K \rightarrow \Delta_{in} \sigma_{in} \equiv \Delta_{in} \gamma; \quad \mu \rightarrow G_{KXX} \quad (22)$$

Thus, there is a correspondence between the Cahn-Hilliard-Hillert and Gibbs theories. It is of interest to show that there is no contradiction between the formulas for the activation energy in the Cahn-Hilliard-Hillert and Gibbs theories.

In fact, the order of accuracy for activation energy is determined by the energy (barrier) necessary for merging particles, which is a product of the particle chemical potential ($-\mu$) and the defect size (linear case implied) and can be estimated via Equation 21.

Finally, it is not difficult to arrive at the following formula:

$$\Delta G \sim (\Delta_{in} \gamma \mu)^{1/2} \quad (23)$$

Therefore, there is no contradiction between the Cahn-Hilliard-Hillert and Gibbs theories.

Conclusions

The formation of electrochemical phase is a typical example of a first-order phase transition. Electrodeposition of nanostructures has been considered in terms of the classical Gibbs and the Cahn-Hilliard-Hillert theories. Agreement between the theories Cahn-Hilliard-Hillert and Gibbs was obtained. We found no contradiction between the theories Cahn-Hilliard-Hillert and Gibbs. We have reviewed the progress of the modern thermodynamic theory of the growth of nanoparticles. We note the existence and of other approaches of the theory, presented for example in [23-26].

References

1. Gibbs JW (1928) Graphical methods in the thermodynamics of fluids. Yale University Press.
2. Frenkel J (1939) Statistical Theory of Condensation Phenomena. J Chem Phys 7: 200.
3. Frenkel J (1955) Kinetic Theory of Liquids. Dover Publications.
4. Zeldovich JB (1943) Acta Physicochim. U.R.S.S. 18: 1.
5. Gamburg Y, Zangari G (2011) Theory and Practice of Metal Electrodeposition. Springer, New York, USA, p: 375.
6. Volmer M, Weber A (1923) Z Phys Chem. (Leipzig) 119: 277.
7. Wagner CZ (1961) Theorie der Alterung von Niederschlagen durch Umlösen (Ostwald Reifung). Electrochem. 65: 581-591.
8. Anisimov MA (1991) Critical Phenomena in Liquids and Crystals. Philadelphia, Gordon & Breach, USA, p: 280.
9. Abraham FF (1974) Homogeneous Nucleation Theory. Academic Press, New York and London.
10. Erdey-Gruz T, Volmer MZ (1931) Phys Chem. 157: 165.
11. Vetter KJ (1967) Electrochemical Kinetics: Theoretical Aspects. Academic Press, New York, USA, p: 726.
12. Landau LD (1937) On the Theory of Phase Transitions 1. Phys Zs Sowjet 11: 26.
13. Landau LD (1937) On the Theory of Phase Transitions 2. Phys Zs Sowjet 11: 545.
14. Ma SK (1976) Modern Theory of Critical Phenomena. Westview Press, USA.
15. Baranov SA (2015) Handbook of Nanoelectrochemistry: Electrochemical Synthesis Methods, Properties and Characterization Techniques. Springer, Switzerland, pp: 1057-1069.
16. Cahn JW, Hilliard JE (1958) Free Energy of a Nonuniform System. I. Interfacial Free Energy. J Chem Phys. 28: 258.
17. Cahn JW (1959) Free Energy of a Nonuniform System. II. Thermodynamic Basis. J Chem Phys 30: 1121.
18. Cahn JW, Hilliard JE (1959) Free Energy of a Nonuniform System. III. Nucleation in a Two-Component Incompressible Fluid. J Chem Phys 30: 688.
19. Cahn JW (1968) Spinodal decomposition. Trans Met Soc AIME 242: 166.
20. Cahn JW, Larche FC (1982) Surface stress and the chemical equilibrium of small crystals-II. Solid particles embedded in a solid matrix. Acta Met 30: 51.
21. Hillert M (1975) Diffusion and interface control of reactions in alloys. Metall Trans. 6: 5.
22. Khachaturyan AG (1983) Theory of Structural Transformations in Solids. Wiley, New York.
23. Schmelzer JWP (2002) In: Encyclopedia of Surface and Colloid Science. Marcel Dekker Inc., New York.
24. Gutzow I, Schmelzer J (1995) The Vitreous State: Thermodynamics, Structure, Rheology, and Crystallization. Springer, Berlin, Germany.
25. Schmelzer JWP, Roepke G, Priezhev VB (1999) Nucleation Theory and Applications. Joint Institute for Nuclear Research Publishing House, Dubna, Russia.
26. Schmelzer JWP, Roepke G, Priezhev VB (2002) Nucleation Theory and Applications. Joint Institute for Nuclear Research Publishing House, Dubna, Russia.