Work of formation of a cluster of a new phase that is in a uniform external electric field and in the field of an ion outside the cluster

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In the framework of the classical thermodynamic approach, an expression for the joint contribution to the work of formation of a spherical cluster of a new phase from the side of a uniform external electric field and the field of an ion that is outside the cluster is obtained. The analysis of the obtained expression in the case of the vapor−liquid phase transition is carried out.

Keywords: nucleation, work of cluster formation, electric field, ions, nucleation rate.

The presence of electric field is a factor affecting the stability of metastable phases and nucleation rate [1,2]. Therefore, the controllable nucleation in electric fields finds application in various technologies, for instance, in obtaining nanoscale particles [3].

In calculating the work of the new-phase cluster formation in the electric field, only two cases are typically considered. In the first case, the cluster is assumed to arise in the ion field [4,5]. In the other one, the cluster is assumed to be formed in a uniform external field [6,7]. However, situations often occur, both in nature and technology, when the new-phase clusters emerge in the simultaneous presence of ions and uniform external electric field. In [8] there was obtained a relation for the work of the new-phase cluster formation for the case when the cluster is formed on the ion in the presence of the uniform external field. This paper considers the case of formation of the new-phase cluster that is located simultaneously in the uniform external field and in the field of the ion outside the cluster. This case is important since in the process of the cluster formation the ion may be driven out to the cluster periphery [9,10].

The main task in calculating the work of the new-phase cluster formation in the electric field is to calculate the electric field contribution to this work. It is possible to show [11,12] that the general expression for the electric field contribution to the work of the new-phase cluster formation looks as follows:

$$W_{el} = \frac{\varepsilon_0}{2}\left(\varepsilon_{old} - \varepsilon_{new}\right) \int\limits_{V_{cl}} \nabla\varphi \cdot \nabla\tilde{\varphi} dV, \qquad (1)$$

where ε_0 is the electrical constant, ε_{old} and ε_{new} are the static dielectric permittivities for the old and new phases, respectively, φ and $\tilde{\varphi}$ are the electric potentials in the absence and in the presence of the cluster, respectively. In (1), the volume integration is performed over the cluster volume V_{cl}. Further we will find parameter W_{el} for the

case considered in this study; for simplicity, assume that the new-phase cluster has a spherical shape.

Let us use the spherical frame of reference with the origin in the center of the spherical cluster (Fig. 1). Axis z with respect to which polar angle θ is counted will be directed along strength **E** of the old-phase uniform electric field.

Based on the superposition principle, potential φ may be defined as

$$\varphi = \varphi_{field} + \varphi_{ion}, \qquad (2)$$

where φ_{field} is the uniform field electrostatic potential in the absence of the cluster, φ_{ion} is the ion field electrostatic potential in the absence of the cluster. In the selected frame of reference, potential φ_{field} is defined as

$$\varphi_{field} = -Er\cos\theta, \qquad (3)$$

while potential φ_{ion} outside the ion may be written as

$$\varphi_{ion} = \frac{q}{4\pi\varepsilon_0\varepsilon_{old}r_p} = \frac{q}{\varepsilon_0\varepsilon_{old}r_0}\sum_{l=0}^{\infty}\sum_{m=-l}^{l}\frac{1}{2l+1}\left(\frac{r}{r_0}\right)^l$$

$$\times Y_{lm}^*(\Omega_0)Y_{lm}(\Omega), \quad r < r_0. \qquad (4)$$

Here r is the distance from the cluster center to observation point P; q is the ion electric charge; r_p is the distance from the ion center to observation point P; r_0 is the cluster center to ion center distance; $Y_{lm}(\Omega)$ are the spherical harmonics; $\Omega \equiv \{\theta, \psi\}$ is the set of spherical angles of the radius-vector drawn from the cluster center to observation point P (ψ is the azimuthal angle); $\Omega_0 \equiv \{\theta_0, \psi_0\}$ is the set of spherical angles of the radius-vector drawn from the cluster center to the ion center. Substituting (3) and (4) into (2), obtain the final expression for potential φ.

The superposition principle allows potential $\tilde{\varphi}$ to be represented as

$$\tilde{\varphi} = \tilde{\varphi}_{field} + \tilde{\varphi}_{ion}, \qquad (5)$$

where $\tilde{\varphi}_{field}$ is the uniform field electrostatic potential in the presence of the cluster, $\tilde{\varphi}_{ion}$ is the ion field electrostatic
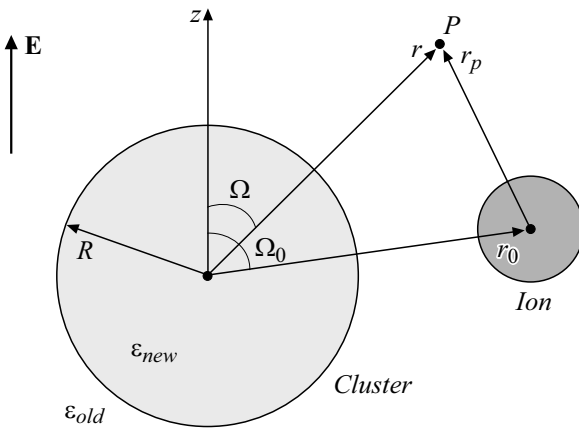
Figure 1. The problem geometry.

potential in the presence of the cluster. It can be shown [13] that

$$\tilde{\varphi}_{field} = -\frac{3\varepsilon_{old}}{2\varepsilon_{old} + \varepsilon_{new}} E r \cos\theta, \quad r \leqslant R, \qquad (6)$$

where R is the cluster radius. In addition, it can be shown [14] that

$$\tilde{\varphi}_{ion} = \frac{q}{\varepsilon_0 r_0} \sum_{l=0}^{\infty} \sum_{m=-l}^{l} \frac{1}{\varepsilon_{old}(l+1) + \varepsilon_{new}l} \left(\frac{r}{r_0}\right)^l$$
$$\times Y_{lm}^*(\Omega_0) Y_{lm}(\Omega), \quad r \leqslant R. \qquad (7)$$

Substituting (6) and (7) into (5), obtain the final expression for potential $\tilde{\varphi}$ inside the cluster.

Taking into account the found potentials φ and $\tilde{\varphi}$, calculate the integral in relation (1). Calculating this integral, take into account that [15]:

$$r\cos\theta = \sqrt{\frac{4\pi}{3}} \sum_{l=0}^{\infty} \sum_{m=-l}^{l} r^l Y_{lm}(\Omega) \delta_{l1}\delta_{m0},$$

$$\nabla r^l Y_{lm}(\Omega) = l r^{l-1} \mathbf{Y}_{lm}^{(-1)}(\Omega) + \sqrt{l(l+1)} r^{l-1} \mathbf{Y}_{lm}^{(1)}(\Omega),$$

where δ_{ij} is the Kronecker delta, $\mathbf{Y}_{lm}^{(-1)}(\Omega)$ and $\mathbf{Y}_{lm}^{(1)}(\Omega)$ are the vectors spherical harmonics. In addition, in calculating this integral, the properties of the spherical harmonics and vectors spherical harmonics should be taken ino account [15]. As a result, obtain the following expression:

$$W_{el} = \frac{(\varepsilon_{old} - \varepsilon_{new})q^2}{8\pi\varepsilon_0\varepsilon_{old}R} \sum_{l=0}^{\infty} \frac{l}{\varepsilon_{old}(l+1) + \varepsilon_{new}l} \left(\frac{R}{r_0}\right)^{2l+2}$$
$$+ \frac{2\pi\varepsilon_0\varepsilon_{old}(\varepsilon_{old} - \varepsilon_{new})R^3 E^2}{2\varepsilon_{old} + \varepsilon_{new}} - \frac{(\varepsilon_{old} - \varepsilon_{new})qR^3 E \cos\theta_0}{(2\varepsilon_{old} + \varepsilon_{new})r_0^2}. \qquad (8)$$

In the absence of the uniform external electric field ($E = 0$), relation (8) transforms into the known equation for the contribution to the work of the new-phase spherical cluster formation from the field of the ion located outside the cluster [5]. In the absence of the ion ($q = 0$), relation (8) transforms into the known equation for the contribution to the work of the new-phase spherical cluster formation from the uniform external electric field [6]. The simultaneous presence of the ion and uniform external electric field means that it is necessary to take into account in relation (8) the cross term depending on angle θ_0.

Fig. 2 presents as an example the calculated dependences of work W of the new-phase cluster formation on the cluster radius R for a polar substance (methanol) in the case of the vapor−liquid phase transition. Those dependences were calculated using relation

$$W = 4\pi\sigma R^2 - \frac{4\pi kT \ln S}{3v}R^3 + W_{el}, \qquad (9)$$

where parameter W_{el} is defined by (8). Here σ is the liquid−vapor surface tension coefficient, k is the Boltzmann constant, T is the temperature, S is the vapor supersaturation, v is the volume per a molecule in the liquid.

Fig. 2 shows that in the case of the vapor−liquid transition the presence of electric field leads to a decrease in the new-phase cluster critical radius R^* that can be found from the $dW(R^*)/dR = 0$ condition and to a decrease in the work of formation of the new-phase cluster with critical size $W^* = W(R^*)$. This, in its turn, results in an increase in the probability of such a cluster formation and, hence, in an increase in the nucleation rate $J \propto \exp(-W^*/kT)$.

Analysis of expression (9) shows that in the case of the vapor−liquid phase transition in the presence of the uniform external electric field and ion located outside the cluster, work W^* significantly depends on angle θ_0 at the fixed distance r_0. The dependence on angle θ_0 manifests itself in the fact that work W^* for the positively charged ion in the uniform external electric field will be maximal at $\theta_0 = 0$ and minimal at $\theta_0 = \pi$ (see curves *4* in Fig. 2). Thereat, work W^* for the negatively charged ion will be maximal
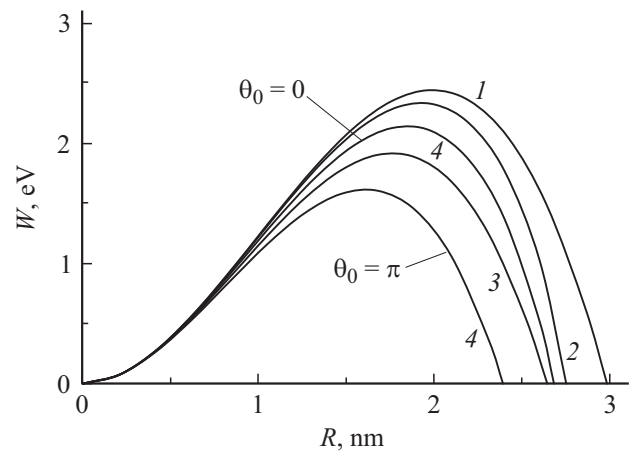

Figure 2. W versus R for methanol in the case of the vapor−liquid phase transition at $T = 280$ K, $S = 1.5$ and $r_0 = 3$ nm. *1* — $q = 0$ and $E = 0$ (homogeneous nucleation), *2* — $q = e$ (e is the electron charge) and $E = 0$, *3* — $q = 0$ and $E = 500$ MV/m, *4* — $q = e$ and $E = 500$ MV/m.

at $\theta_0 = \pi$ and minimal at $\theta_0 = 0$. Thus, the probability of the critical-size new-phase cluster formation in the case of a positively charged ion will be maximal at $\theta_0 = \pi$, while that in the case of a negatively charged ion will be maximal at $\theta_0 = 0$.

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Conflict of interests

The author declares that he has no conflict of interests.

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