

Heterogeneous nucleation on partially wettable charged conducting seed particle

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The currently widely used model for ion-induced nucleation assumes complete spherical symmetry of the system, implying that the seed ion is immediately surrounded by the condensing liquid from all sides. This theory, although giving a rough picture of the observed behaviour, fails to fully reproduce experiments.

We apply a thermodynamically consistent formalism (Nishioka and Kusaka, 1992; Debenedetti and Reiss, 1998) to calculate the reversible work needed to form a dielectric liquid nucleus of a new phase on a charged insoluble conducting sphere within a uniform macroscopic one- or multicomponent mother phase. Compared with widely used ion-induced nucleation theory we take a step further and treat more realistic geometries, where a cap-shaped liquid cluster forms on the surface of the seed particle. The spherical symmetry is lost. We consider the formation energy of an embryo constrained to have fixed volume and shape. The bulk and surface phases of constrained embryo and its environment are in thermodynamic equilibrium, but not necessarily with each other. Electrostatic energy of the system is found as an energy that is required to carry electric charge from infinity to a seed particle or, alternatively, the energy of electrostatic field generated by this charging process. At charging the seed is either bare or has a constrained embryo on it. We limit ourselves to a linear relationship between dielectric displacement and electric field strength.

In nucleation theory a real system is replaced with a hypothetical system where bulk properties differently from the real system preserve their values up to dividing surfaces between bulk phases. Usually certain location of dividing surfaces (e.g. surfaces of tension) and values of coefficients like the coefficients of surface and line tensions are chosen so that free energies of hypothetical and real systems coincide. In the neutral case differences in energy densities of systems occur only in transition zones. We assume that the location of dividing surfaces assures also that the difference in total electrostatic energies evoked by differences in dielectric properties of real and hypothetical systems can be ignored. Unlike neutral system, in the charged systems the difference in electrostatic energy densities manifest itself over the entire extent of systems. This makes the introduction of excess quantities more complicated. We show that the assumption concerning the coincidence of electrostatic energies is valid with a relative uncertainty of the order of the ratio of the width of transition zone between bulk phases to the size of an embryo. We take into account also the possibility that the molecules in the surface

layers can be spontaneously permanently polarized, and introduce the surface and line excess polarizations. The surface excess polarization is the electrical potential difference of a hypothetical system through the double layer charge distribution at the dividing surface. The line excess polarization describes the effect of seed particle charge and the polarization of triple line zone on the line tension. This excess quantity is proportional to the charge of the seed and it is additional to the line tension of uncharged system.

The expression of the formation energy of a constrained embryo is varied and the extremity condition for a critical embryo found. The equalities of chemical potentials of each species between the nucleus and the vapour represent the conditions of chemical equilibrium. The generalized Young equation that relates contact angle with surface tensions, surface excess polarizations and line tension containing also the electrical contribution from triple line excess polarization expresses the condition of mechanical equilibrium at three-phase contact line. The generalized Laplace equation gives the condition of mechanical equilibrium at vapour-liquid interface: it relates generalized pressures in neighbouring bulk phases at an interface with surface tension, excess surface polarization and dielectric displacements in neighbouring phases with two principal radii of surface curvature and curvatures of equipotential surfaces in neighbouring phases at that point. We re-express also the generalized Laplace equation as a partial differential equation, which, along with electrostatic Laplace equations for bulk phases, determines the shape of a nucleus. Finally, we derive expressions that are suitable for calculations of the size and composition of a critical nucleus (generalized version of the classical Kelvin-Thomson equation).

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