



A Theory of Condensation on Soluble Surfactant Nuclei

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We have obtained relationships which describe in an analytical form the influence of the surface activity of the matter in soluble condensation nuclei and the influence of nucleus size on the value of the vapour chemical potential at the threshold for barrierless nucleation.

Finding a value of the vapour chemical potential at the threshold for nucleation without encountering a thermodynamic barrier is a central problem in the thermodynamics of condensation on soluble nuclei. The threshold value is determined by a maximum (or by the largest of the maxima if there are several maxima) of the chemical potential of the condensate, *i.e.* the substance condensing in the droplet out of the vapour.

In the case of surface-inactive matter in condensation nuclei, the threshold value of the vapour chemical potential was found by Köhler.¹ Since for macroscopic nuclei which are able to promote condensation at low vapour supersaturations and, from this point, are of the largest practical interest, a maximum in the chemical potential of the condensate corresponds to droplets with a low concentration of nuclear matter dissolved,²

so ignoring adsorption of nuclear matter onto the droplet surface is justified in the case of the surface-inactive matter of nuclei. However, the adsorption is significant, even at low solution concentrations, in the case of surfactant nuclei. The influence of adsorption on the surface tension of the droplet is also pronounced in this case. One aim of this communication is to take into account the effects of adsorption of surfactant matter in condensation nuclei when determining the maximum value of the chemical potential of the condensate.

Consider a droplet formed on soluble condensation nuclei from a vapour. The droplet consists of a liquid solution of the nuclear matter in the condensate. Let v be the number of condensate molecules in the droplet and v_n be the number of nucleus molecules. We suppose the temperature T of the droplet to be equal to the temperature of the surrounding vapour-gas medium. The droplet is in mechanical equilibrium with the vapour-gas medium: the pressure inside the droplet is the sum of capillary pressure and the external pressure created by the vapour-gas medium (the latter is much smaller than the capillary pressure and we will neglect it).

We denote R as the radius of the equimolecular (with respect to the condensate) dividing surface for the droplet and x_n the concentration of nuclear matter dissolved in the bulk of the droplet. The quantity x_n is expressed in terms of molar parts. We then suppose that inequality (1) is valid over the whole theoretical range of R . Inequality (1) sets² a lower limit on the value of v_n , the external theoretical parameter, excluding from consideration the case $v_n \sim 1$.

$$x_n < 1 \tag{1}$$

With inequality (1) fulfilled, radius R almost coincides with the radius of tension surface and is concerned with the number of condensate molecules in the droplet, v , as $v = 4\pi R^3/3v$ where v is the condensate molecular volume. The fact that the solution in the droplet is diluted with respect to the component coming from the nucleus also means complete dissociation of the nuclear matter (if it is an electrolyte).

From the above, we have for μ , the chemical potential of the condensate in the droplet, equation (2),

$$\mu = \mu_\infty - ikTx_n + 2\sigma v/R \tag{2}$$

where μ_∞ is the chemical potential of pure condensate at the flat interface between liquid and vapour, k is Boltzmann's constant, i is the number of ions formed as a result of dissociation of one molecule of the matter of nucleus (for a non-electrolyte, $i=1$) and σ is the droplet surface tension. Note that the diluteness of the solution of nuclear matter always guarantees small electrical corrections (if the nuclear matter is an electrolyte) to equation (2) by comparison with the non-electrical contributions present in equation (2).

The chemical potential of the condensate, μ , achieves its maximum at the point $R=R_0$ where $\partial\mu/\partial R|_{R=R_0}=0$. Then, according to equation (2), we have (at $R=R_0$) equation (3).

$$[-ikT + (2v/R)(\partial\sigma/\partial x_n)](\partial x_n/\partial R) - (2\sigma v/R^2) = 0 \tag{3}$$

Denoting as Γ_n the adsorption of the nuclear matter on the droplet surface, we obtain from the balance of nuclear matter equation (4).

$$x_n = 3v(\nu_n - 4\pi R^2\Gamma_n)/4\pi R^3 \tag{4}$$

Differentiating both sides of the equation (4) with respect to R and using the equality $\partial\Gamma_n/\partial R = (\partial\Gamma_n/\partial x_n)(\partial x_n/\partial R)$, we obtain equation (5).

$$\partial x_n/\partial R = -(3v/4\pi R^4)(3\nu_n - 4\pi R^2\Gamma_n)/[1 + (3v/R)(\partial\Gamma_n/\partial x_n)] \tag{5}$$

The dependence of surface tension, σ , on solution concentration in the bulk of a droplet is determined by the Gibbs adsorption equation. Based on equation (1), this equation has the form in equation (6).

$$\partial\sigma/\partial x_n = -ikT\Gamma_n/x_n \tag{6}$$

The set of equations (2)–(6) is complete on adding an adsorption isotherm: $\Gamma_n = \Gamma_n(x_n)$. This set may be solved, even in its general form.

Variable R_0 can be changed for a dimensionless variable, equality (7),

$$z \equiv 4\pi R_0^2\Gamma_n/\nu_n \tag{7}$$

which represents a fraction of the condensation nuclear matter adsorbed on the droplet surface at the maximum chemical potential of the condensate. From equations (7) and (4) at $R=R_0$, equations (8) and (9) follow.

$$R_0 = (3v\Gamma_n/x_n)(1-z)/z \tag{8}$$

$$\nu_n^{1/3} = (6\pi^{1/2}v\Gamma_n^{2/3}/x_n)(1-z)/z^{2/3} \tag{9}$$

Setting $R=R_0$, $\mu \equiv \sigma/ikT\Gamma_n$ and using equations (4)–(8), we transform equation (3) to equation (10).

$$(3-z)^2 - 2uz[1-z+z(\partial\ln\Gamma_n/\partial\ln x_n)] = 0 \tag{10}$$

At the same time, substituting equation (8) into equation (2) gives equation (11).

$$\mu|_{R=R_0} = \mu_\infty + ikTx_n[2uz/3(1-z) - 1] \tag{11}$$

Solving equation (10) as a quadratic equation in z gives equation (12).

$$z_{\pm} = \frac{u + 3 \pm \{u|u - 12 + 18(\partial\ln\Gamma_n/\partial\ln x_n)\}^{1/2}}{1 + 2u - 2u(\partial\ln\Gamma_n/\partial\ln x_n)} \tag{12}$$

From equation (6) the right-hand side of equation (12) may be explicitly defined as a function of x_n or Γ_n (the appropriate choice depends on the specific view of the adsorption isotherm). Indices + and – for z will then correspond to two branches of dependence of z on variable x_n (or Γ_n).

Choosing x_n (or Γ_n) as an independent variable for the description of a droplet at a maximum value of the chemical potential of the condensate we find, with the aid of equations (12) and (11), the corresponding z and $\mu|_{R=R_0}$. As a next step, we assign, by means of equations (8) and (9), values of R_0 and ν_n to the quantity $\mu|_{R=R_0}$ found. In this way, the total picture of the influence of surface activity of the matter in soluble condensation nuclei and the influence of their size on the maximum value of the chemical potential of the condensate and on the threshold value of the vapour chemical potential is described in an analytical form.

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