

The Effect of the Surface Activity of Soluble Condensation Nuclei on the Thermodynamics of Heterogeneous Nucleation in Vapours

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The influence of the surface activity of nuclear matter on the vapour chemical potential at the threshold of barrierless heterogeneous nucleation has been analysed taking into account the lateral interactions in the adsorbed monolayer of nuclear matter on the drop surface; the results obtained are valid within a wide size range for a condensation nucleus soluble in the drop arising on the nucleus from a vapour.

Data on 'critical' vapour supersaturation, at which the process of heterogeneous nucleation in a vapour proceeds rather intensively, are the most important experimental information available on the nucleation activity of condensation nuclei. At a macroscopic nucleus size, critical supersaturations lie in an extremely narrow range and practically coincide with the threshold value of vapour supersaturation above which the process of heterogeneous nucleation no longer requires the overcoming of an energy barrier. The case of heterogeneous nucleation on the nuclei of soluble surfactants is especially interesting and complex since a surfactant exhibits its influence not only through its solubility, but also through its surface activity. A general approach to this problem was elaborated earlier.¹ Here we complement it by using an adsorption isotherm equation, which will allow us to consider the case of several extremes of the condensate chemical potential and the influence of lateral interactions in the adsorbed monolayer of nuclear matter on the drop surface.

The threshold vapour supersaturation is known to be related to the threshold value of the vapour chemical potential which, in its turn, is determined by the maximum value of the chemical potential of the condensate in its drop. In the case of surfactant nuclei, the maximum of the condensate chemical potential can be found from rigorous thermodynamic formulae.¹ Using these in combination with an adsorption isotherm equation, we can analyse the influence of the surface activity of condensation nuclear matter (soluble in a drop arising from a vapour) on the threshold value of the vapour chemical potential and, hence, on the critical vapour supersaturation. We choose the Frumkin adsorption isotherm² which is representative with respect to many soluble surfactants and takes into account lateral interactions between surfactant molecules. Although the Frumkin adsorption isotherm permits us to take into account also phase transitions in an adsorbed monolayer, we are interested only in the region where lateral interactions are not so strong and where phase transitions are still impossible.

Let x be the mole fraction of dissolved nucleus surfactant in the solution inside a drop, and Γ the surfactant adsorption at the drop surface. The Frumkin adsorption isotherm equation is:

$$x/x_\alpha = [\Gamma/(\Gamma_\infty - \Gamma)] \exp(-2\kappa\Gamma/\Gamma_\infty) \quad (1)$$

where x_α and Γ_∞ are positive parameters representing the characteristic values of the mole fraction and adsorption, respectively. Lateral interactions in the adsorbed monolayer are described by the positive parameter κ . The monolayer state is always stable at $\kappa < 2$, whereas at $\kappa > 2$ there is an unstable state region dividing different phase states of the monolayer. The existence of such instability regions for soluble surfactant monolayers was confirmed experimentally.³

Let v_0 be the number of condensate molecules in a drop at which the condensate chemical potential attains its extreme value μ_0 . The latter may be represented in the form:¹

$$\mu_0 = \mu_\infty + 6\pi^{1/2}kTv_l \frac{\Gamma_\alpha^{3/2}}{v_n^{1/2}z^{3/2}} \left(\frac{2\sigma z}{3kT\Gamma} + z - 1 \right) \quad (2)$$

where μ_∞ is the condensate chemical potential value corresponding to the equilibrium of the condensate with vapour at their flat interface, k is the Boltzmann constant, T is the temperature of the drop and the surrounding vapour-gas medium, v_l is the molecular volume of condensate, v_n is the number of molecules or ions of a condensation nucleus completely dissolved in the drop, z is the fraction of adsorbed nuclear matter at the drop surface with respect to its total amount in the drop, and σ is the drop surface tension. The quantities Γ , σ and z refer to an extreme of the condensate chemical potential. According to the adsorption isotherm, equation (1), we have the following expression for the drop surface tension:

$$\sigma = \bar{\sigma} + kT\Gamma_\infty \left[\ln \left(1 - \frac{\Gamma}{\Gamma_\infty} \right) + \kappa \left(\frac{\Gamma}{\Gamma_\infty} \right)^2 \right] \quad (3)$$

where $\bar{\sigma}$ is the surface tension of a drop of a pure condensate.

According to the algorithm described earlier,¹ it is possible to relate μ_0 and v_0 to quantity v_n at given parameters $\bar{\sigma}$, Γ_∞ , x_α and κ . In the case of a surface inactive nuclear matter, such a relationship produces a unique value: there exists a single extreme (a maximum) of the condensate chemical potential for every given value of v_n .⁴ However, the surface activity of nuclear matter can lead to the coexistence of three values of μ_0 and v_0 , i.e. to the coexistence of three extremes (two maxima and a minimum) of the condensate chemical potential in some regions of parameters $\bar{\sigma}$, Γ_∞ , x_α , κ and quantity v_n . Then the threshold value of the vapour chemical potential, μ_{th} , will be determined by the largest of the maxima μ_0 . The value of v_0 corresponding to this maximum is denoted as v_{th} .

The influence of surface activity of soluble condensation nuclei on μ_{th} and v_{th} is conveniently expressed through the quantities:

$$f^{(\mu)} \equiv \frac{(\mu_{th} - \mu_\infty)}{(\bar{\mu}_{th} - \mu_\infty)}$$

and

$$f^{(v)} \equiv \frac{v_{th}}{\bar{v}_{th}}$$

where the barred values refer to the absence of adsorption of the nuclear matter as in the case of soluble surface-inactive nuclear matter. Using equation (2) and the formulae for v_{th} , $\bar{\mu}_{th}$ and \bar{v}_{th} obtained earlier,^{1,4} we can write $f^{(\mu)}$ and $f^{(v)}$ in the form:

$$f^{(\mu)} = \frac{1}{2} (9\kappa T\Gamma/2\bar{\sigma}z)^{3/2} \left(\frac{2\sigma z}{3kT\Gamma} + z - 1 \right) \quad (4)$$

$$f^{(v)} = (2\bar{\sigma}z/9kT\Gamma)^{3/2} \quad (5)$$

The dependence of quantities $f^{(\mu)}$ and $f^{(v)}$ on $\lg v_n$ computed following the algorithm described earlier¹ and using equations (1)–(5) are presented in Figs. 1 and 2.

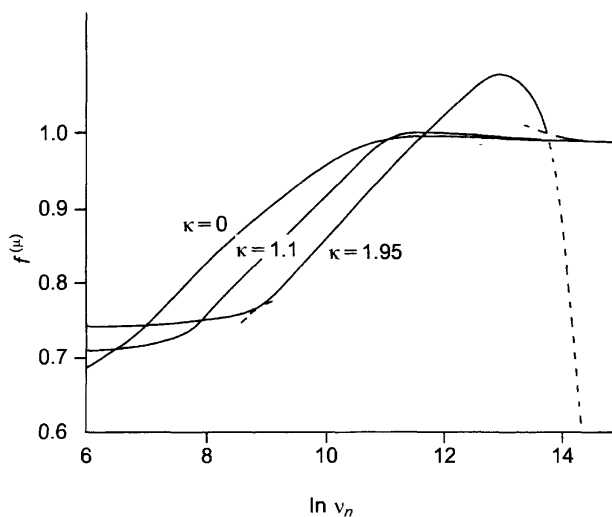


Fig. 1 The dependence of quantity $f^{(u)}$ on $\lg v_n$ in the case of the Frumkin adsorption isotherm at $\bar{\sigma}/kTT_\infty = 15$, $\Gamma_\infty = 2 \times 10^{18}$ molecule m^{-2} , $v_l = 3 \times 10^{-29}$ m^3 , $x_\alpha = 10^{-5}$ and $\kappa = 0, 1.1, 1.95$.

It is sufficient to set the parameters $\bar{\sigma}/kTT_\infty$, v_l , x_α and κ for use in calculations. It was set in calculations $\bar{\sigma}/kTT_\infty = 15$, $\Gamma_\infty = 2 \times 10^{18}$ molecule m^{-2} , $v_l = 3 \times 10^{-29}$ m^3 and $x_\alpha = 10^{-5}$. The three values $\kappa = 0$, $\kappa = 1.1$ and $\kappa = 1.95$ were taken for the lateral interaction parameter. The values chosen for parameters $\bar{\sigma}/kTT_\infty$, Γ_∞ , v_l , x_α and κ are not only realistic, but also appropriate to illustrate both the simple situation when the condensate chemical potential possesses a single maximum at every value of the variable $\lg v_n$, and more complex situations when there is a region or even two regions in the $\lg v_n$ -axis where two maxima of the condensate chemical potential coexist.

The behaviour of quantities $f^{(u)}$ and $f^{(v)}$ corresponding to the absolute maximum of the condensate chemical potential is depicted in Figs. 1 and 2 by solid lines. To make the picture complete, broken lines depict the behaviour of quantities $(\mu_0 - \mu_\infty)/(\bar{\mu}_{\text{th}} - \mu_\infty)$ and v_0/\bar{v}_{th} corresponding to the smaller of two coexisting maxima of the condensate chemical potential. It is seen that the curve of $f^{(u)}$ has no break points and the curve of $f^{(v)}$ has no points of discontinuity at $\kappa = 0$ when the Frumkin adsorption isotherm changes to the Langmuir one. Then the condensate chemical potential has a single maximum. At $\kappa = 1.1$, the curve of $f^{(u)}$ has a break and the curve of $f^{(v)}$ has a discontinuity at the point where $\lg v_n = 7.8$. At $\kappa = 1.95$, the curve of $f^{(u)}$ has breaks and the curve of $f^{(v)}$ has discontinuities even at two points where $\lg v_n = 8.9$ and $\lg v_n = 13.6$. The replacement of the absolute maxima of the condensate chemical potential occurs at the break points in the curve of $f^{(u)}$ and at the points of discontinuity in the curve of $f^{(v)}$. The occurrence of these points gives evidence of joint existence of two maxima of the condensate chemical potential. Remarkably, such a coexistence is possible not only in the absence of phase transitions (as was said above), but also in the absence of lateral interactions themselves. As was shown earlier,⁵ such a coexistence takes place also at $\kappa = 0$ if, however, the quantity $\bar{\sigma}/kTT_\infty$ is large enough to exceed the critical value 15.23.

The quantities $f^{(u)}$ and $f^{(v)}$ tend to limiting values independent of v_n , both on the right and left parts of the $\lg v_n$ -axis corresponding to two different extreme situations. The right part of the $\lg v_n$ -axis corresponds to the situation when the adsorption of nuclear matter at the drop surface is very far from saturation and the limiting value for $f^{(u)}$ and $f^{(v)}$ is unity. The left part of the $\lg v_n$ -axis corresponds to the situation when almost all the nuclear matter has been

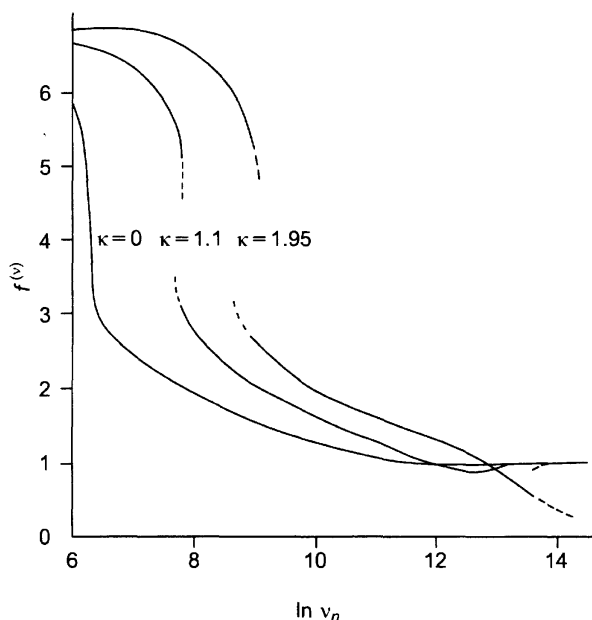


Fig. 2 The dependence of quantity $f^{(v)}$ on $\lg v_n$ in the case of the Frumkin adsorption isotherm at $\bar{\sigma}/kTT_\infty = 15$, $\Gamma_\infty = 2 \times 10^{18}$ molecule m^{-2} , $v_l = 3 \times 10^{-29}$ m^3 , $x_\alpha = 10^{-5}$ and $\kappa = 0, 1.1, 1.95$.

adsorbed at the drop surface, the limiting value for $f^{(u)}$ is smaller and for $f^{(v)}$ is much larger than unity.

The non-monotonous behaviour of $f^{(u)}$ shown in Fig. 1, as noticeable even at $\kappa = 0$, is of especial attention. Due to such behaviour, there are in the $\lg v_n$ -axis both a region where $f^{(u)} > 1$, i.e. $\mu_{\text{th}} > \bar{\mu}_{\text{th}}$, and a region where $f^{(u)} < 1$, i.e. $\mu_{\text{th}} < \bar{\mu}_{\text{th}}$. Hence, the surface activity of nuclei can not only increase, but also decrease the threshold value of vapour supersaturation. In other words, surface activity is able not only to make the nucleation process in a vapour more difficult, as is generally accepted, but also to make it easier.

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