Condensation on macroscopic nuclei at low dynamic supersaturations of the vapour phase

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We have found analytically the total number of super-critical drops nucleating in the vapour phase on macroscopic condensation nuclei under conditions of gradual creation of the vapour metastable state.

Macroscopic condensation nuclei are of interest to us in this communication in view of their ability to initiate vapour condensation at small vapour supersaturations. The same interest in dynamic, *i.e.* gradual, externally adjustable, creation of the vapour metastable state is determined by the fact that gradual creation allows us to control the development of the condensation process and even to operate it. Both the macroscopic condensation nuclei and the gradual creation of the vapour metastable state are common in nature. As a basis for the following, we will use the nucleation thermodynamics of super-critical drops on macroscopic condensation nuclei. The thermodynamics is most elaborate[1,2] in the case when macroscopic condensation nuclei are soluble in drops condensing on them and when the nuclear matter is surface-inactive. We will restrict ourselves just to this case. As a basis for the following, we will also use kinetics of heterogeneous condensation under conditions of gradual creation of the vapour metastable state.[3,4] The important new result of this communication consists in finding how the total number of super-critical drops formed on macroscopic condensation nuclei depends on the parameters of the vapour and liquid phases, and how this number is associated with the parameters of condensation nuclei and of the rate of external creation of the vapour metastable state. The condensation nuclei are supposed to be identical. It will be noted at the end of the communication how the proposed theory can be generalised in the case of polydisperse macroscopic nuclei.

Let us denote as ν_n the number of molecules (or ions) in the condensation nucleus. At macroscopic size of nuclei we have $\nu_n^{1/3} >> 1$. At this size the sizes of nucleating, and moreover, nucleated super-critical drops, will be so large[2] that the solution of the nuclear matter within the drops is dilute. Let n stand for the number of vapour molecules per unit volume of the vapour-gas medium and n_∞ be the number of saturated vapour molecules per the unit volume. Let us define the vapour supersaturation ζ as $\zeta = (n/n_\infty) - 1$.

The supersaturation threshold value ζ_{th} above which the nucleation of super-critical drops proceeds barrierlessly on the condensation nuclei in the vapour is already expressed, as obtained earlier,[1,2] as

$$\zeta_{\text{th}} = 2(2a)^{3/2}/(27\nu_n^{1/2}), \tag{1}$$

where $a \equiv (4\pi\sigma/kT)(3v/4\pi)^{2/3}$, where σ and v are the surface tension and the volume per molecule in the condensing liquid, k is the Boltzmann constant and T the temperature of the drops and surrounding vapour-gas medium. As follows from (1) and $\nu_n^{1/3} >> 1$, we have $\zeta_{\text{th}} << 1$.

Let us denote as n_{tot} the total number of molecules of the condensing substance per unit volume of the vapour-gas medium, including molecules within drops. Let us define the ideal supersaturation Φ as $\Phi = (n_{\text{tot}}/n_\infty) - 1$. Development of the condensation process can be controlled from the outside by assignment of the law of growth of ideal supersaturation with time. Evidently, the ideal supersaturation Φ cannot be less than the real supersaturation ζ (allowing for vapour intake by drops).

Let us present the vapour supersaturation ζ in the form

$$\zeta = \zeta_{\text{th}}(1 - \varepsilon), \tag{2}$$

where ε is the deviation from the threshold value ζ_{th}. In the sub-threshold range of supersaturations where $0 < \zeta < \zeta_{\text{th}}$ and correspondingly $0 < \varepsilon < 1$, the work of drop formation from the vapour onto the nucleus has a well and a potential hump. The height drop between the well and the hump gives the activation energy of nucleation. We will express the energy in energy units kT and denote it as F. The drops become super-critical, *i.e.* grow irrepressibly, only if they overcome the activation barrier. Expression (3) was obtained earlier[2]

$$F = (16/6^{1/2})\nu_n \varepsilon^{3/2} \tag{3}$$

for the activation energy in the case of macroscopic condensation nuclei.

If vapour supersaturation is such that heterogeneous nucleation proceeds already sufficiently intensively but, however, requires to overcome an activation barrier, the activation energy F lies (almost irrespective of the value of the initial concentration of condensation nuclei) in the interval $3 < F < 30$. According to (3) we have in this interval

$$\varepsilon^{1/2} \simeq \nu_n^{-1/3}, \tag{4}$$

where we set, with sufficient accuracy, $(6^{1/2}F/16)^{1/3} \simeq 1$. We will call 'pre-threshold' the range of supersaturations in which double inequality $3 < F < 30$ and, correspondingly, equality (4) hold. At $\nu_n^{1/3} >> 1$ (for nuclei of macroscopic size) the pre-threshold range fills, as is seen from (4), an extremely narrow slit in the sub-threshold range $0 < \varepsilon < 1$ and has a thickness of the order of the distance of the slit from the upper boundary of the sub-threshold range.

The total number of nucleated super-critical drops is a feature of primary importance for the condensation process. At this value Φ_* of the ideal supersaturation Φ, at which the one-half of the total number of super-critical drops has appeared, is significant. The value Φ_* is not known in advance under the conditions of gradual creation of the vapour metastable state. The more correct the value, the more correct the total number of nucleating super-critical drops predicted by the theory.

Let us define the dimensionless parameter Γ as

$$\Gamma = -\Phi_*(\partial F/\partial\zeta)\big|_{\zeta = \Phi_*}. \tag{5}$$

This parameter characterises the strength of the dependence of the activation energy F on supersaturation ζ in the vicinity of the point $\zeta = \Phi_*$.

Under the assumption that the vapour metastable state is not created too quickly, the value Φ_* of the ideal supersaturation lies in the pre-threshold range of supersaturations. In view of (2), (4) and $\nu_n^{1/3} >> 1$, we have approximately

$$\Phi_* \simeq \zeta_{\text{th}}. \tag{6}$$

The accuracy of the equality (6) derived for the nuclei of macroscopic size is sufficient for a subsequent determination of quantities with a weak power-law dependence on Φ_*.

As shown previously,[5] when the sizes of macroscopic condensation nuclei are not too large, drops overcome the activation barrier in a free-molecular regime of material exchange between the drops and the vapour. Let us suppose that this regime is also preserved for the largest super-critical drops formed in their effective nucleation stage. Then, to describe the growth of the super-critical drops, it is convenient to use the linear ‘size’ of the drop, ρ, scaled in such way that ρ^3 is equal to the number of condensate molecules in a drop. Almost immediately after formation of the super-critical drop, size ρ increases in time with a rate $\dot{\rho}$ independent of the size and determined as

$$\dot{\rho} = \alpha\zeta/\tau. \qquad (7)$$

Here α is the condensation coefficient for vapour molecules and $\tau \equiv 12/[(36\pi)^{1/3}\upsilon^{2/3}n_\infty \upsilon_\mathrm{T}]$ is the characteristic time for the molecular free path in a saturated vapour. The quantity $\upsilon^{2/3}$ estimates the cross-section of collisions of vapour molecules, the quantity υ_T equals the mean thermal velocity of the molecules.

We will consider the following power-law approximation to the dependence of the ideal supersaturation Φ on time t,

$$\Phi = (t/t_\infty)^m, \qquad (8)$$

serves as representative of a description of the external creation of a vapour metastable state. The approximation has two independent positive parameters: the scaling time t_∞ and the power index m. The time t is counted off the moment at which the approximation (8) gives $\Phi = 0$.

In effect, we need approximation (8) only at the stage of effective nucleation of super-critical drops, when the relative change in the ideal supersaturation is small, and thus the approximation (8) is fully justified. As for the preceding preliminary stage of creation of the vapour metastable state, when the super-critical drops have not yet appeared, the law of growth of the ideal supersaturation Φ can deviate at this stage from the law given by approximation (8).

Consideration of the correlation between the vapour intake and consumption of condensation nuclei by super-critical drops, having a rate of external increase of ideal supersaturation in the course of time, is of primary importance in the kinetic theory of heterogeneous condensation in the gradual creation of the vapour metastable state. The consideration was performed earlier[3,4] irrespective of the size of the condensation nuclei. On these grounds, recognising equalities (5), (7) and (8), we have for the total number N of super-critical drops nucleated per unit volume of the vapour-gas medium

$$N = \eta[1 - \exp(-1/h)] \qquad (9)$$

where the dimensionless quantity h is given as

$$h = 6(\eta/n_\infty)[(\alpha t_\infty/m\tau)^3 1/\Gamma^2]\Phi_*^{(2m+3)/m} \qquad (10)$$

and η is the initial concentration of condensation nuclei (their number per unit volume of the vapour-gas medium at the beginning of effective nucleation of super-critical drops).

Taking into account the macroscopic size of the nuclei and expanding (10), which is expressed in powers of Φ_*, with the help of (6), using in this (1)–(5), we obtain

$$h \simeq 2^{-4}(2^{5/2}/27)^{(2m+3)/m}(\eta/n_\infty)(\alpha t_\infty/m\tau)^3 \times$$
$$\times a^{(6m+9)/2m}/\nu_n^{(14m+9)/6m}. \qquad (11)$$

Formulae (9) and (11) express in an analytical form the number N, the most important characteristic of the condensation process, in terms of parameters n_∞, α, τ and a of the vapour and condensing liquid, the parameters η and ν_n of condensation nuclei and the parameters m and t_∞ of the rate of external creation of the vapour metastable state. All the parameters mentioned, which can be easily calculated from experimental data, are fundamental to the proposed condensation theory. A high sensitivity, shown by the formulae (9) and (11), of the number N to the rate of external creation of vapour metastable state (to parameters m and t_∞) confirms that one can control the development of the condensation process and even to operate it under conditions of gradual creation of the vapour metastable state. The fact that nucleation of the super-critical drops under these conditions occurs within the pre-threshold range of vapour supersaturations which lies, according to (1), (2), (4) and $\nu_n^{1/3} >> 1$, at very low levels, confirms the ability of the macroscopic nuclei to initiate vapour condensation at low vapour supersaturations.

If the initial concentration of nuclei η is so high that, in view of (11) and (9), we have $h >> 1$ and $N = \eta/h$, then only a few nuclei will be the centres of formation of the super-critical drops (each super-critical drop captures only one nucleus). If the initial concentration of nuclei η is so small that, in view of (11) and (9), we have $h << 1$ and $N = \eta$, then practically all these nuclei will become the centres of nucleation of the super-critical drops. Thus the cessation of effective nucleation of the super-critical drops is caused in the limiting situations $h >> 1$ and $h << 1$ by vapour and, correspondingly, by condensation nuclei intake by these drops.

Due to the narrowness of the pre-threshold range of vapour supersaturations, in the case when the initial condensation nuclei are polydisperse, only that part of the initial spectrum of nuclear sizes, which is adjacent to the upper boundary of the spectrum and is very narrow in relative thickness (of the order of $\nu_n^{-2/3}$), is responsible for effective nucleation of the super-critical drops. Generalisation of the proposed theory will not be difficult in this case. We only need to consider η as the sum of the concentration of nuclei in the upper part of the initial spectrum of nuclear sizes.

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References

1 H. Kohler, *Trans. Faraday Soc.*, 1936, **32**, 1152.

2 F. M. Kuni, A. K. Shchekin and A. I. Rusanov, *Kolloidn. Zh.*, 1993, **55**, 34 (*Colloid J.*, 1993, **55**, 174).

3 A. P. Grinin, F. M. Kuni and V. B. Kurasov, *Kolloidn. Zh.*, 1990, **52**, 430 [*Colloid J. USSR* (*Engl. Transl.*), 1990, **52**, 371].

4 A. P. Grinin, F. M. Kuni and V. B. Kurasov, *Kolloidn. Zh.*, 1990, **52**, 437 [*Colloid J. USSR* (*Engl. Transl.*), 1990, **52**, 377].

5 F. M. Kuni, A. K. Shchekin and A. I. Rusanov, *Kolloidn. Zh.*, 1993, **55**, 45 (*Colloid J.*, 1993, **55**, 184).

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