Ostwald ripening on the wall of a semi-infinite system

R. Burghaus*
Institut für Theoretische Physik IV, Heinrich Heine Universität Düsseldorf, Universitätsstraβe 1, 40225 Düsseldorf, Germany
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The Lifshitz-Slyozov-Wagner theory of Ostwald ripening describes the asymptotic ($t\rightarrow\infty$) diffusive growth of the condensate in a supersaturated solution. In the present work this theory is extended to a semi-infinite system where droplets of the condensate exist in the bulk as well as on the boundary wall. Both types of droplets interact with each other via the bulk diffusion field. We focus on the implications of this interaction for the growth of surface droplets which in the partial-wetting regime are spherical caps. It turns out that these droplets show a qualitatively different behavior for contact angles bigger or less than $\pi/2$. In the former case the droplets may initially grow but eventually shrink until the boundary wall becomes completely dry. The latter case is dominated by droplets which grow and eventually cover the whole wall. Within our model the growth rate of droplets with an arbitrary contact angle is calculated exactly. [S1063-651X(96)02312-4]

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Lifshitz, Slyozov, and independently Wagner have established a theory for the precipitation of the condensate in a supersaturated solution [1]. They considered an unbounded system in which nuclei of the condensate are formed by fluctuations. Supercritical nuclei then grow via diffusion of the molecules in the solution. For a small degree of supersaturation the number density of droplets is small, and consequently a single-droplet picture can be used. The growth of the supercritical droplets reduces the supersaturation (conservation of matter) and in this way leads to an increase of the critical radius. It then happens that small supercritical droplets can get surpassed by the critical radius, i.e., they become subcritical and eventually die out, so that large droplets grow at the expense of the small ones. The main results of this theory are the asymptotic time dependence of the critical radius $a_{\mathrm{cr}}\propto t^{1/3}$, the growth rate of supercritical droplets, and the late-time distribution of droplets.

In the present work the Lifshitz-Slyozov-Wagner theory is extended to semi-infinite systems, where in a supersaturated state droplets of the condensate nucleate in the bulk as well as on the boundary wall. The growth properties of both types of droplets is determined by their mutual interaction via the bulk diffusion field. In the following we are interested in the effect of this interaction on the growth behavior of the surface droplets. This situation is different from the one encountered in the discussion of breath figures [2]. There the growth of surface droplets is due to a constant particle flow towards the wall combined with a two-dimensional diffusion on the wall.

In the physical situation that we address the diffusive approach to thermal equilibrium is considered at constant temperature in the partial wetting or dewetting regime of the system [3]. In addition we assume that the relaxation processes driven by the surface tension of the droplets are fast compared to the bulk diffusion process. Then droplets on the wall will always have the form of a spherical cap with a time-dependent radius $a(t)$ but a constant contact angle θ, obeying Young's relation. Due to mass conservation the condensate will coexist with the solvent in the eventual equilibrium state.

A basic ingredient of the Lifshitz-Slyozov theory is the equation of motion for the radius of a spherical bulk droplet,

$$\frac{da}{dt}=D[c_\infty-c_{\mathrm{s}}(a)]\frac{1}{a}, \tag{1}$$

where D means the diffusion constant of the condensate molecules in the solution, $c_\infty(t)$ their volume concentration at infinity, and $c_{\mathrm{s}}(a(t))$ the equilibrium concentration close to the droplet surface. Due to mass conservation $c_\infty(t)$ decreases during the process of precipitation. The concentration $c_{\mathrm{s}}(a)$ is given by the Gibbs-Thomson relation

$$c_{\mathrm{s}}(a)=c_0\left(1+\frac{2\Lambda}{a}\right), \tag{2}$$

where $c_0\equiv c_\infty(\infty)$ is the equilibrium concentration on a planar surface and Λ is a capillary length.

In the derivation of (1) it has been assumed that the concentration field $c(x,t)$ adiabatically follows the droplet growth and accordingly obeys the Laplace equation $\Delta c=0$ with Dirichlet boundary conditions c_∞ and $c_{\mathrm{s}}(a)$. This allows us to understand Eq. (1) in terms of an electrostatic analogy (apparently already observed by Maxwell, see Ref. [4]), where the droplet surface is considered as the electrode of a capacitor. Then $Dc(x)$ can be identified with the electric potential, and the diffusion flux $D\partial_\perp c(x)$ through the droplet surface with the surface charge density multiplied by 4π. Integration of the latter quantity over the droplet surface shows that the growth rate of the droplet volume corresponds to the droplet charge. Therefore, Eq. (1), after multiplication with $a^2/3$, resembles the relation $Q=CU$ between the charge $Q=1/3(da^3/dt)$, the capacity $C=a$, and the voltage $U=D[c_\infty-c_{\mathrm{s}}(a)]$.

The case of a growing surface droplet on the boundary wall of the system can be treated in a similar way [4]. One now has to determine $c(x)$ from the Laplace equation with Dirichlet conditions $c=c_\infty$ at infinity, $c=c_{\mathrm{s}}(a)$ at the droplet

*Electronic address: burghaus@uni-duesseldorf.de

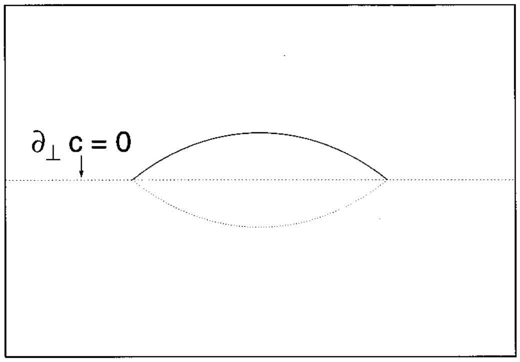

FIG. 1. The spherical cap at the boundary wall and its mirror image.

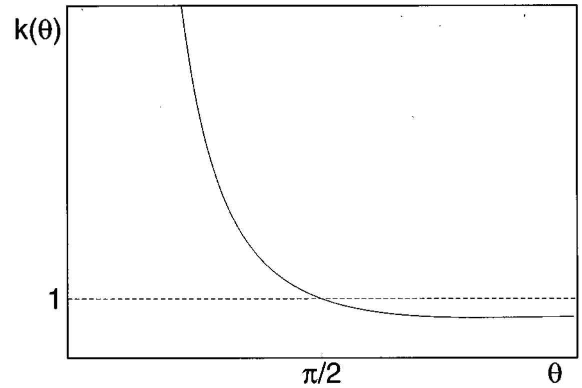

FIG. 2. Plot of the function $k(\theta)$.

surface, and the additional Neumann condition $\partial_\perp c=0$ along the boundary wall representing the condition of zero diffusion flux into the wall. This problem can be solved by the method of mirror charges which automatically takes care of the Neumann condition (see Fig. 1). Then, in the above argument one has to replace the volume V and the capacity C of the sphere by the corresponding quantities $\tilde{V}$, $\tilde{C}$ of the lens in Fig. 1. As a result one finds the equation of motion [4]

$$\frac{da}{dt}=kD[c_\infty-c_s(a)]\frac{1}{a}, \tag{3}$$

where

$$k=\frac{\tilde{C}}{C}\frac{\partial V/\partial a}{\partial \tilde{V}/\partial a}. \tag{4}$$

Explicitly

$$\tilde{V}(a,\theta)=\tfrac{2}{3}\pi[1-\cos(\theta)]^2[2+\cos(\theta)]a^3 \tag{5}$$

and

$$\tilde{C}(a,\theta)=a\frac{\sin(\theta)}{2(\pi-\theta)}\left\{\pi-8\sum_{m=1}^{\infty}\sin^2\left(\frac{m\pi}{2}\right)\right.\times\left[\psi\left(m+\frac{1}{2}\right)-\psi\left(\frac{m\pi}{2(\pi-\theta)}+\frac{1}{2}\right)\left.+\ln\left(\frac{\pi}{2(\pi-\theta)}\right)\right]\right\}, \tag{6}$$

with $\psi(\alpha)$ meaning the logarithmic derivative of Euler's function [5]. These expressions reduce to V and C for $\theta=\pi/2$, in agreement with the fact that the lens of Fig. 1 then becomes a sphere. As a consequence k is a function of θ only, with $k(\theta=\pi/2)=1$ (see Fig. 2). Therefore, the growth properties of surface droplets with a contact angle $\theta=\pi/2$ are identical to those of the corresponding bulk droplets. In terms of the critical radius

$$a_{\mathrm{cr}}(t)=\frac{2\Lambda c_0}{c_\infty(t)-c_0}. \tag{7}$$

Equation (3) can be rewritten in the form

$$\frac{da}{dt}=\frac{2\Lambda kDc_0}{a}[a_{\mathrm{cr}}(t)^{-1}-a(t)^{-1}], \tag{8}$$

which at $a=a_{\mathrm{cr}}$ shows a transition from a shrinking to a growing droplet. The critical radius a_{cr} is independent of θ and therefore identical to that of bulk droplets. Moreover, the time dependence of $c_\infty(t)$, and consequently of $a_{\mathrm{cr}}(t)$, is the same as in an unbounded system because in the thermodynamic limit the contribution of the droplets far from the wall dominates.

Following the procedure in the Lifshitz-Slyozov approach, Eq. (3) now is rewritten in terms of the dimensionless quantities $\tau=3\ln a_{\mathrm{cr}}(t)/a_{\mathrm{cr}}(0)$, $u(\tau)=a(t)/a_{\mathrm{cr}}(t)$ and $\gamma=6D\Lambda c_0/d_t a_{\mathrm{cr}}{}^3(t)$ as

$$\frac{du^3}{d\tau}=\gamma k(\theta)(u-1)-u^3. \tag{9}$$

The crucial idea behind this transformation is the observation that $\gamma(\tau)$ approaches a fixed point value $\gamma_0=27/4$ for $\tau\to\infty$ which via the definition of γ implies the asymptotic behavior $a_{\mathrm{cr}}(t)\propto t^{1/3}$.

In the bulk case ($k=1$) the special value γ_0 corresponds to the situation shown in Figure 3(b) where the arrows indicate the behavior of the function $u(\tau)$. Figures 3(a) and 3(c) describe an unlimited shrinking or growth of droplets which in the bulk case both contradict mass conservation. Accordingly only the limiting behavior $\gamma(\tau)\to\gamma_0$ from below is admissible for $k=1$ [1].

Since due to its definition $\gamma(\tau)$ is the same function for bulk and for surface droplets, γ can be replaced by γ_0 in Eq. (9). Then Figs. 3(a) and 3(c) correspond to $k(\theta)<1$ and $k(\theta)>1$, i.e., to surface droplets with a contact angle $\theta>\pi/2$ and $\theta<\pi/2$, respectively. This time, these cases are

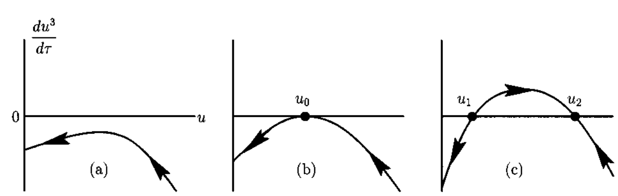

FIG. 3. Plot of Eq. (9): (a) $\gamma k<\gamma_0$; (b) $\gamma k=\gamma_0$; (c) $\gamma k>\gamma_0$.

not in conflict with mass conservation to which the surface droplets do not contribute in the thermodynamic limit. In Fig. 3(a) the variable u runs to $u=0$ which implies that for a contact angle $\theta>\pi/2$ the surface droplets shrink away until the wall eventually becomes dry. This happens, even if initially the droplet radius has exceeded the critical radius, because the latter grows more rapidly and eventually takes over the actual radius. For $\theta<\pi/2$ Fig. 3(c) applies with a stable fixed point u_2, so that surface droplets with $a>u_1 a_{\mathrm{cr}}$ grow until (after merging together) the wall is completely wetted. Since generally $u_1>1$, it may happen also in this case that an initially supercritical droplet (with $a_{\mathrm{cr}}<a<u_1 a_{\mathrm{cr}}$) becomes subcritical and eventually dies out.

In the Lifshitz-Slyozov theory of the infinite system [1] it is easy to find the late-time distribution of bulk droplets. Its derivation is closely related to the properties of the dynamics near the fixed point u_0 of Fig. 3(b). For surface droplets with $\theta>\pi/2$ there is no fixed point which can stabilize an asymptotic droplet distribution. As already pointed out, for $\theta<\pi/2$ all droplets inevitably merge together and eventually form a homogeneous wetting layer. In the exceptional case $\theta=\pi/2$ Fig. 3(b) applies so that the asymptotic droplet distribution is identical to that of the Lifshitz-Slyozov theory [1].

Within our model Eqs. (3)–(6) represent the exact result for the growth rate of surface droplets with an arbitrary contact angle. It implies that asymptotically the wall of the system can become dry or covered by a layer of the condensate. This is not in conflict with mass conservation since the bulk acts as a reservoir which eats or feeds the surface droplets, respectively. Although these droplets accordingly are unstable, we mention that in practice their lifetime may be very large.

In comparing our results with reality one has to keep in mind several limitations of our model. Most importantly, if the system has a wetting transition, our theory does not apply asymptotically close to the transition point since there $\theta=0$ so that the growth rate (3) diverges. This, however violates our basic assumption that the growth process is slow compared to the relaxation processes driven by surface tension. The possible appearance of a dynamic contact angle, e.g., due to a surface roughness of the wall [6], also has not been taken into account.

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