Drop Formation on Insoluble Particles

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Nucleation of liquid from the vapor is a process of drop formation. When condensation does not proceed according to a nucleation process, another explanation for the formation of drops is required. In this paper it is shown that an adsorbed monolayer contains enough liquid to account for the number of droplets observed in condensation experiments. Furthermore it is shown that there are no thermodynamic objections against spontaneous drop formation on an adsorbed layer as a result of continued adsorption at a critical saturation ratio. An experiment is cited as evidence for drop formation on insoluble aerosol particles without nucleation.

INTRODUCTION

Usually condensation of liquid on insoluble surfaces is treated as a nucleation process but this results in great discrepancies between the actual value and the theoretical value of the minimal saturation ratio at which drop formation is observed (1). Therefore it has been recommended that condensation on insoluble surfaces be regarded as an adsorption process in which the liquid is deposited on the substrate as a layer. In that case the radius of curvature of the liquid–vapor interface must have a finite value at the initial stage of condensation and this allows comparatively low values of the critical saturation ratios. This concept was shown to be supported by experimental observations (1) and it was concluded that drop formation must be considered apart from adsorption as a liquid–liquid transition. This transition is the subject of the present paper.

CONDENSATION ON PARTICLES

We can distinguish three classes of condensation on particles depending on the molecular interaction between the material of the particle and the liquid.

(1) When the particle is soluble the interaction is considered to be strong. In the case where the particle dissolves completely the interface disappears and it is impossible to determine a contact angle. Liquid–vapor equilibrium is represented by a Köhler curve (2) as shown in Fig. 1 curve b. A condition for unlimited drop growth is that the saturation ratio S exceeds a critical value S_{crit} which is determined by the maximum of the Köhler curve for condensation on a soluble particle.

(2) When the interaction is weak the particle does not dissolve. Adsorption and drop formation on the particle are both possible; there is a liquid–particle interface, and a contact angle θ can be determined. Now the liquid–vapor equilibrium is represented by curve c in Fig. 1, but only the extremes of this curve, i.e., the end where $S \rightarrow 0$ and the other end where $S \rightarrow 1$, are completely determined by general thermodynamic arguments. The curve itself and in particular S_{crit}, the maximum value, depends on the strength of the interaction between the liquid and the substrate (1).

(3) An intermediate class between strong and weak interaction is presented by condensation on an already existing drop of the same

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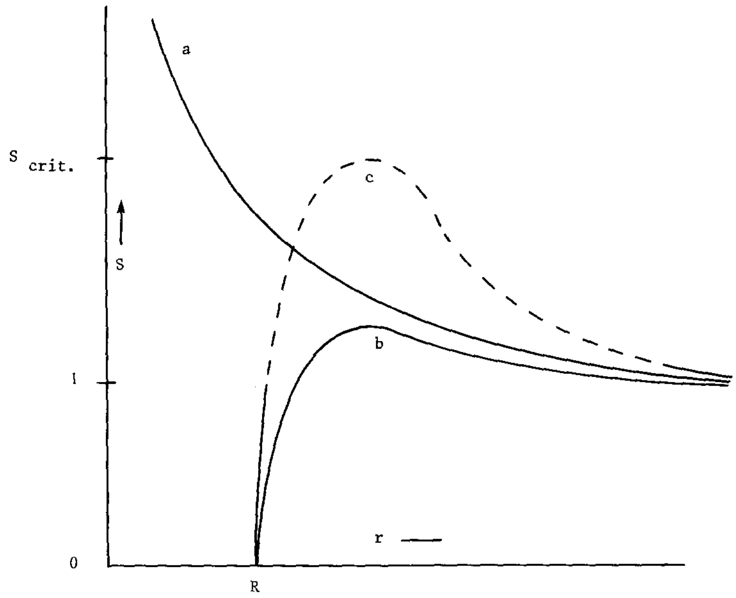

FIG. 1. (a) Kelvin curve; (b) Köhler curve; (c) condensation on insoluble particle with radius R.

liquid. Here cohesive interaction in the liquid is identical to the adhesion between the newly condensed envelope and the original drop. There is no interface and $\theta = 0$. This intermediate class is nothing else but homogeneous condensation, illustrated by the Kelvin curve a, in Fig. 1.

The Kelvin curve represents the equilibrium at the interface of a drop with radius r and its own vapor at the saturation ratio $S(r)$ according to

$$S(r) = \exp\{2M\sigma/\rho RTr\} \qquad [1]$$

where M, σ, and ρ, respectively, represent the molar mass, the specific free surface energy, and the mass density of the liquid, and T = temperature, R = universal gas constant.

For water at 293K, and measuring r in nanometers:

$$S(r) \simeq e^{1.1/r}. \qquad [2]$$

With regard to drop formation the curves a and c in Fig. 1 are relevant. Curve a determines the chemical potential of the liquid in the drop and curve c is in fact an adsorption isotherm on a curved surface, determining the chemical potential of the liquid in the condensed layer around the particle. Drop formation must depend on the relation between these potentials.

To explain drop formation at low supersaturations we must assume that the maximum S_{crit} of curve c lies very close to (within 0.1%) of the Kelvin curve. This important assumption will be illustrated in the following sections but first we must discuss the concept of a liquid drop in relation to bulk liquid and to adsorbed liquid.

ADSORPTION ISOTHERMS

In condensation studies we are concerned with adsorption at saturation ratios near unity. A typical adsorption isotherm can be imagined as a continuous curve, starting at $t = 0$, $S = 0$, and approaching the asymptote $S = 1$ for $t \rightarrow \infty$. Here, the amount of material adsorbed on a unit surface is expressed by t, the thickness of the adsorbed layer. The idea is that a thick plane–parallel layer of liquid has bulk properties and must, by definition be in equilibrium with vapor at $S = 1$. Theoretical examples of this typical shape are the BET isotherm, type II, and the FHH isotherm (3). These representations can be misleading because they suggest that a bulk liquid layer may grow from an adsorbed layer in a continuous way, whereas in reality that is generally not the case. A macroscopic layer can only exist when the contact angle θ of the liquid on the substrate is zero. In all other cases where $\theta > 0$, a bulk layer is an artificial concept. What is thought to be a layer is actually a large drop deformed by gravity or other external forces. Consequently, when $\theta > 0$ we must discard the idea of a bulk layer with large values of t, and we must accept that the adsorption isotherms breaks off at a critical value of t; $t_c \ll \infty$. This was already suggested by Derjaguin and Zorin in 1957 (4).

Further condensation results in a situation where vapor must coexist with both an adsorbed layer and droplets, consequently $S(r) > 1$ for $t = t_c$. This is not a postulate but an observation: it is an every day experience that a thin layer of water breaks up into drops on most surfaces. And although the relative humidity may appear to be below 100% during that experience, the actual saturation ratio in the immediate vicinity of the drop must be above unity due to evaporation of water from the curved surface.

Now consider the equilibrium of a drop with radius r on an adsorbed layer of thickness t in equilibrium with vapor of saturation ratio S. The drop geometry is determined by the equilibrium of forces along the solid surface as shown in Fig. 2. This equilibrium is expressed by Young's law which is abbreviated here to

$$\sigma_{lv} \cos \theta = \sigma_a. \qquad [3]$$

σ_{lv} is the surface tension of the bulk liquid–vapor interface and σ_a is an effective surface tension which tends to spread the drop. Usually σ_a is expressed as $\sigma_{sv} - \sigma_{sl}$, the difference between the specific free surface energies of respectively the solid–vapor interface and the solid–liquid interface.

Assuming that σ_{lv} and θ are constants, i.e., independent of S and r, σ_a must be a constant.

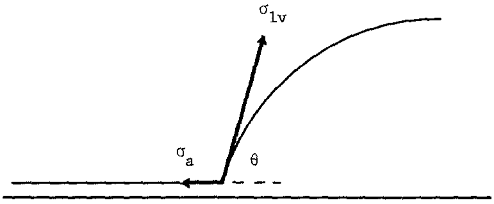

FIG. 2. Young's law for a drop with contact angle θ on an adsorbed layer.

However when $t > t_c$ the adsorbed liquid achieves bulk properties, the surface tension changes from σ_a to σ_{lv}. We can try to understand this by assuming t_c to be the working range of the van der Waals adhesion forces between the substrate and the liquid. When $t < t_c$, molecular motions in the layer are restricted by these forces but when $t > t_c$, the molecules at the top of this layer no longer feel these restrictions, they can move as in a bulk liquid and consequently they form a liquid drop.

Pashley (5) has shown that on hydrophobic surfaces the critical thickness of an adsorbed waterlayer can be as large as 10 nm for values of θ between 20 and 80°.

DROP FORMATION ON A SPHERICAL PARTICLE

Thermodynamic aspects of drop formation from an adsorbed layer are demonstrated conveniently on a spherical surface. Afterward the situation on a plane substrate can be treated as a limiting case of the spherical situation.

We shall consider a spherical particle with radius R covered with an adsorbed layer of thickness t, forming a complete sphere with radius $r = R + t$.

At first sight it would seem that a continuous transition from the curved adsorbed layer t to a bulk liquid sphere $r = R + t$ must be possible because during all stages of condensation $\Delta r = \Delta t$. But a closer consideration will show that a continuous transition according to curve c in Fig. 1 is impossible. Starting at $r = R$ the equilibrium curve c in Fig. 1 approaches the

Kelvin curve a. First strongly because the adhesive interaction in a thin layer strongly decreases the chemical potential of the liquid in the adsorbed layer. At the particular stage of growth where the Kelvin curve is crossed the chemical potential of the liquid equals the chemical potential in a pure drop of the same radius, i.e., the influence of the adhesive interaction on the chemical potential in the liquid is zero. Further growth along curve c in Fig. 1 would imply that with t increasing steadily, the adhesion begins to work again but now with a positive sign: short range adhesion changes to long range repulsion. This absurd implication is introduced by our attempt to comply with the requirements for equilibrium between the curved adsorbed layer and the vapor for every value of r and every value of t; $S = S(r) = S(t)$ while $\Delta r = \Delta t$. An acceptable solution requires one extra degree of freedom, and this is granted when t and r can vary independently, i.e., when drops appear on the curved adsorbed layer like they do on a plane adsorbed layer.

In correspondence with the considerations in the preceding section we now ascribe a constant surface tension σ_a to the adsorbed layer in the thickness range $0 < t < t_c$. After exceeding the critical thickness, the surface tension changes to σ_{lv} and the liquid starts flowing to form a drop with a contact angle θ on the adsorbed layer around the particle. At this stage we are confronted with three interesting aspects of drop formation which will be discussed separately here.

Flow Rate

In the initial stage of drop formation, liquid flow is restricted to the top monolayer of the envelope. Due to viscosity the flow rate must be extremely low. The problem which rises here is analogous to that in the classical theory of heterogeneous nucleation on an insoluble surface (2). One of the weak spots in that theory is the calculation of a nucleation rate, which is the number of visible drops appearing from the vapor on a unit surface in unit time. Application of the molecular kinetic theory of gases results in calculated values of the nucleation rate, many orders of magnitude smaller than the observed values. Pound *et al.* (6) saved the theory by suggesting that the nucleating drops received their supply not only directly from the vapor but also by surface diffusion along the substrate, which was assumed to be a very effective process. Here adsorption sneaks in through the back door after it had been explicitly dismissed from condensation theory by Bangham and Razouk (7).

In the present study we are not directly concerned with this problem. We have discarded the nucleation concept and so we do not require a nucleation rate or a related kinetic parameter at this moment.

Thermodynamics of Drop Formation on a Spherical Particle

Figure 3 shows the initial stage 1 and a later stage 2 of drop formation on a particle with radius R. We assume an ambient saturation ratio $S \geqslant S(r)$, where $S(r)$ is the equilibrium value of S for a liquid–vapor interface with a surface curvature determined by r. Consequently the drop cannot evaporate in stage 2, nor in the intermediate stages between 1 and 2 where the radius of curvature decreases steadily from the value $(R + t_c)$ to r (we temporarily neglect the effect of condensation). This steady decrease can be illustrated by visualizing drop formation in an alternative way as an extrusion process during which the particle is gradually forced out of the liquid envelope, preserving its adsorbed layer. Initially $\theta = 0$, and the final stage is reached when the contact angle has achieved its equilibrium value. In the most unfavorable case with regard to drop formation, i.e., when we neglect the effects of further condensation, the radius of curvature of the liquid envelope will decrease from $(R + t_c)$ to r as the particle emerges. Note the crucial difference with a nucleation process: during nucleation the drop radius must increase from 0 to r.

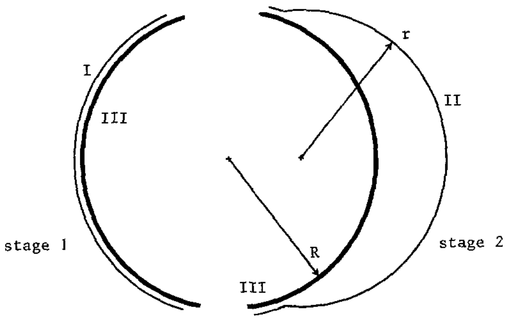

FIG. 3. Stage 1: an adsorbed layer on a spherical particle with radius R. Stage 2: a drop with radius r has formed. I = surface covered with adsorbed layer in stage 2. II = outer surface of the droplet in stage 2. III = surface covered by adsorbed layer in stage 1.

We must now prove that the postulated extrusion process actually occurs when $S \geqslant S(r)$. This requires an investigation of the variation in Gibbs free energy of the system, consisting of vapor (v), adsorbed liquid (a), and bulk liquid (l) during the simultaneous occurrence of condensation and extrusion:

$$\Delta G = \Delta G\,(\text{condensation}) + \Delta G\,(\text{extrusion}). \quad [4]$$

The first RHS term in Eq. [4] is always negative or zero because $S \geqslant S(r)$ and $S \geqslant S(t_c)$. Therefore $\Delta G < 0$ when ΔG (extrusion) < 0.

The free energy of extrusion can be calculated from data presented in Fig. 3, applying the abbreviated version of Young's law as given by Eq. [3]. Starting from an initial stage where the spherical particle with a surface area III is completely covered with a layer which is ready to produce a droplet because it has just grown to a thickness with bulk surface tension σ_{lv}, we reach a new stage (see Fig. 3) where part of the bulk layer has been skimmed to produce a drop. The skimmed surface area is given by I and it has a new surface tension σ_{a} while the liquid–vapor interface of the drop has an area II and bulk surface tension σ_{lv}. The free energy of extrusion ΔG_{e} is then given by $G_2 - G_1$ where G_2 and G_1 are the surface free energies in, respectively, the new stage and the initial stage.

$$\begin{aligned} G_2 &= \mathrm{I}\cdot\sigma_{\mathrm{a}} + \mathrm{II}\cdot\sigma_{\mathrm{lv}} \\ G_1 &= \mathrm{III}\cdot\sigma_{\mathrm{lv}} \\ \hline \Delta G_{\mathrm{e}} &= (\mathrm{I}\cos\theta + \mathrm{II} - \mathrm{III})\sigma_{\mathrm{lv}} \end{aligned} \quad [5]$$

Note that in Eq. [5] $G_1 = \mathrm{III}\cdot\sigma_{\mathrm{lv}}$ and not $\mathrm{III}\cdot\sigma_{\mathrm{a}}$ because in the first stage of drop formation the adsorbed liquid has already achieved the bulk state.

It can be shown that for $t_c \ll R$, $\Delta G_{\mathrm{e}} = 0$ for $\theta = 0$ and $\Delta G_{\mathrm{e}} < 0$ for $\theta > 0$. The general derivation is quite extensive, but for the special case where $r \ll R$ which interests us here in particular,

$$\begin{aligned} \mathrm{I} &\cong 4\pi R^2 - \pi r^2(1 - \cos^2\theta) \\ \mathrm{II} &\cong 2\pi r^2(1 - \cos\theta) \\ \mathrm{III} &= 4\pi R^2 \end{aligned}$$

$$\begin{aligned} \Delta G_{\mathrm{e}} &\simeq (\cos\theta - 1)\cdot\{4\pi R^2 \\ &\quad + (\cos^2\theta + \cos\theta - 2)\pi r^2\}\cdot\sigma_{\mathrm{lv}} \end{aligned}$$

$$\Delta G_{\mathrm{e}} \simeq (\cos\theta - 1)\cdot 4\pi R^2\cdot\sigma_{\mathrm{lv}} \quad [6]$$

which is negative for $\theta \neq 0$.

On a plane surface n drops appear per unit surface and each drop receives its supply of liquid from an area $1/n$; Eq. [6] must then be modified to

$$\Delta G_{\mathrm{e}} \simeq (\cos\theta - 1)\cdot n^{-1}\cdot\sigma_{\mathrm{lv}} \quad [7]$$

which is negative for every value of $n > 0$ when $\theta \neq 0$.

The thickness of the extra layer Δt, deposited on top of t_c will determine the spacing of the drops. When n drops with a contact angle θ appear on 1 m^2 then

$$\alpha\Delta t = n\cdot\frac{\pi r^3}{3}\cdot f(\theta) \quad [8]$$

here, $0 < \alpha < 1$ is the fraction of the surface that was covered by the extra layer and $f(\theta) = 2 - 3\cos\theta + \cos^3\theta$.

Figure 4 shows drop formation of water on a polyethylene ribbon. This experiment was performed in a small thermal diffusion chamber under a normal microscope. The optical resolution was not better than a few micrometers but nevertheless it was possible to observe

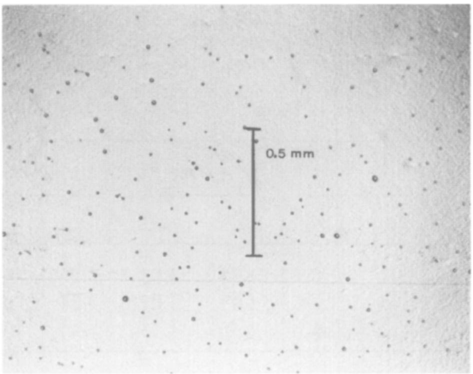

FIG. 4. Water droplets, 30 sec old, on a polythene ribbon in a thermal diffusion chamber at a supersaturation $\leqslant 0.1\%$.

smaller drops due to their sudden appearance in the field of vision as black spots (centers of optical scattering). Under the circumstances of this experiment, $1 < S_{\text{crit}} < 1.001$, so according to Eq. [2] the drop size must have been equivalent to $r > 1$ μm. After the drops had grown to sizes of about 0.1 mm the ribbon was rotated over 90° and the contact angles were measured by means of a rotating eyepiece on the microscope. We found $92° < \theta < 96°$ corresponding to $2.15 < f(\theta) < 2.36$. Drop spacing was of the order of $n = 10^8$ m^{-2}. Then, substituting $f(\theta) = 2.36$ in Eq. [8] results in

$$\alpha \Delta t > 2.36 \times 10^{-10} \text{ m}. \qquad [9]$$

The thickness τ of a monolayer of liquid can be found from the molar volume and Avogadro's number. For water

$$\tau \simeq 3 \times 10^{-10} \text{ m}. \qquad [10]$$

Consequently we can state that one complete monolayer on top of the adsorbed layer is sufficient to allow for the number and size of the observed drops at the extremely low value of $1 < S_{\text{crit}} < 1.001$.

At a supersaturation of 1%, $S = 1.01$ and according to Eq. [2] water drops with $r = 0.1$ μm can exist. From Eq. [8] we found that under those conditions one thousandth of a complete monolayer would contain enough water for 100 droplets per mm^2.

We have repeated these experiments many times on various hydrophobic surfaces, liquid as well as solid, and water drops never failed to appear at a saturation ratio of about 1.001. Therefore we feel justified in assuming that $S(t_c)$, the value of S at which the adsorbed layer becomes unstable on a plane substrate, must be below 1.001 for all hydrophobic materials.

CRITICAL SATURATION RATIO

The result of the preceding section is derived under the conditions that the ambient saturation ratio S allows the equilibrium or the growth of an adsorbed layer with thickness t on a particle with radius R, $S > S(t)$, as well as the existence of droplets with radius r, $S > S(r)$. As we are unacquainted with the value of $S(t)$ we are forced to make an assumption here which must be verified by experiments later. We assume that $S(t)$ for the adsorbed layer on a particle with radius R is very close to $S(R)$, the equilibrium value of S for a drop with radius R. Initially $r < R \rightarrow S(r) > S(R)$ and therefore $S \geqslant S(r)$ remains the only condition for drop formation.

To find $S(r)$ for some specific values of R and θ, consider a droplet with volume V on a spherical particle with radius R (see Fig. 5). Assume again that $t_c \ll R$ and that the droplet

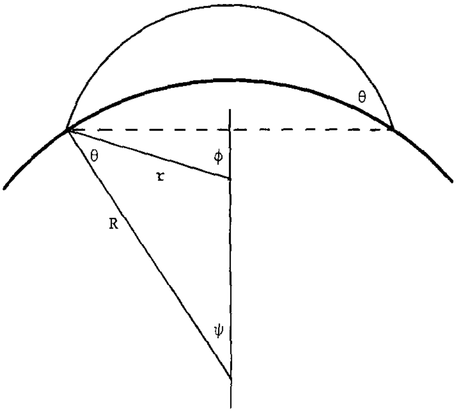

FIG. 5. A drop with radius r and contact angle θ on a spherical particle with radius $R + t_c$, $R \simeq R + t_c$ because $t_c \ll R$.

is formed by the contraction of one complete monolayer, τ, which enveloped the particle. Then

$$V = 4\pi R^2 \tau. \qquad [11]$$

From Fig. 5

$$V = \frac{\pi r^3}{3}(2 - 3\cos\phi + \cos^3\phi) - \frac{\pi R^3}{3}(2 - 3\cos\psi + \cos^3\psi) \qquad [12]$$

and

$$\phi = \theta + \psi \qquad [13]$$

$$r = R\sin\psi/\sin\phi. \qquad [14]$$

From these equations [11], [12], [13], and [14] we have calculated values of the drop radius r for $\tau = 0.3$ nm and for three values of R. The results are presented in Table I. Note that the outer radius r of the resulting droplet is of the same order of magnitude as R of the original particle for all values of θ in this size range below $R = 100$ nm. Consequently we expect that the critical saturation ratio for drop formation on a small particle depends strongly on R and only slightly on θ. Substitution of the r values from Table I in Eq. [2] results in critical values for the saturation ratio $S(r)$ necessary for drop formation on the insoluble particles. These are presented in Table II together with the values S_n, calculated by Fletcher (8) for corresponding cases of heterogeneous nucleation on insoluble particles. The $S(r)$ values are maximum values, representing the most unfavorable case for drop formation with $t_c \ll R$, where τ is only one monolayer and where the effect of continuing deposition of more liquid from the vapor during drop formation is neglected. We are now able to describe the complete condensation process on an insoluble particle with a uniform spherical surface as follows (see Fig. 6).

TABLE I

The Radius in Nanometers of a Single Drop, Grown from One Complete Monolayer with $\tau = 0.3$ nm, Enveloping a Spherical Particle with Radius R nm, for Various Contact Angles

R	$\theta = 0°$	$\theta = 40°$	$\theta = 90°$
100	100	42	24
28	28	16	10
9	9.3	8.3	4.9

TABLE II

Critical Saturation Ratio's for Condensation of Water on Insoluble Particles with Radius R and Contact Angle θ[a]

	$\theta = 0°$		$\theta = 40°$		$\theta = 90°$	
R	S_n	$S(r)$	S_n	$S(r)$	S_n	$S(r)$
100	1.01	1.01	1.35	1.03	3.59	1.05
28	1.04	1.04	1.49	1.07	3.84	1.12
9	1.13	1.13	1.56	1.13	>4	1.25

[a] S_n, according to the nucleation theory; $S(r)$, according to the present paper.

Adsorption proceeds on the particle with radius R according to curve c until $S = S(t_c)$, then drops are generated with radius r and drop growth proceeds along curve a, if $S > S(r)$.

When $S(t_c)$ is very close to the Kelvin curve or when $r > R$, which may occur for very small values of R, then it is possible that $S_{crit} = S(r) < S(R)$, a possibility which is totally inconsistent with nucleation theory.

DROP FORMATION ON SURFACE IMPERFECTIONS

When a droplet grows on a hydrophylic contamination of a hydrophobic substrate, the equilibrium of surface forces and the drop geometry are different from that in Fig. 2. First because the hydrophylic site need not have a circular shape and secondly because the drop does not have a constant contact angle. Unlike the situation sketched in Fig. 2, the drop's boundary is not free to move along the substrate because it is defined by, and even identical to, the boundary of the site. Outside the site $\theta > 0$ and we shall assume that inside the site $\theta = 0$. In this case the development of r during drop growth is similar to the devel-

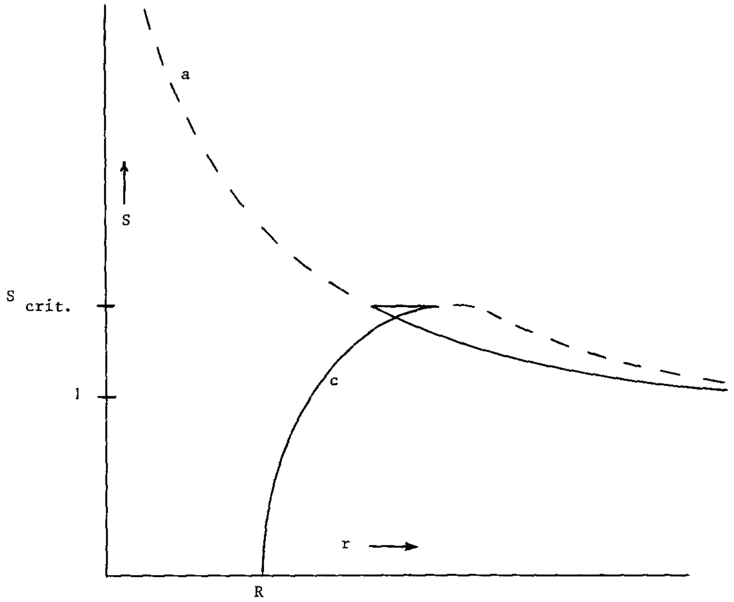

FIG. 6. Condensation and drop formation on an insoluble particle with radius R. The process proceeds along the drawn parts of curves c and a. Note that here, $S_{\text{crit}} < S(R)$ because the maximum of curve c lies close enough near curve a (see also Fig. 1).

opment of r during the extrusion process. Initially the curvature of the liquid–vapor interface is identical to the curvature of the substrate as determined by R.

For a plane surface $r_0 = R = \infty$. As the droplet starts to grow θ increases but the drop radius decreases. On a plane substrate this continues until the droplet forms a complete hemisphere; then r is equal to $\mathbf{r}$ the radius of the hydrophylic site which is now assumed to be circular. From then on, further condensation will cause r to increase again. This implies that the equilibrium saturation ratio for the droplet with $r = \mathbf{r}$ must be the critical saturation ratio for drop formation on a hydrophylic site with $\theta = 0$ and with a diameter of $2\mathbf{r}$ and, according to Eq. [2] when we are considering the condensation of water:

$$S_{\text{crit}} = e^{1.1/\mathbf{r}} \qquad [15]$$

with $\mathbf{r}$ in nm.

The assumption of a hydrophylic site with $\theta = 0$ could in practice correspond to a micropore in the substrate, filled with capillary water on which further condensation proceeds. But in other cases the interaction between water and the site surface can be much stronger, e.g., when the site surface consists of molecular groups of a strong polar nature (10). In those cases S_{crit} may have a lower value than predicted by Eq. [15].

Simultaneously with drop formation on the site, the adsorbed layer develops around it and obscures the sharp boundary of the site where θ changes so suddenly. There may be situations where the drop's base is free to expand over the obscured boundary before the hemispherical shape has been attained. This would be another cause for S_{crit} to have a lower value than predicted by Eq. [15].

DROP FORMATION ON REAL PARTICLES

The surface of a real particle is usually not spherical, not smooth and not homogeneous in a chemical sense. Condensation of water on surface imperfections, e.g., capillary condensation or condensation on surface contaminations of a polar nature, has been studied by various authors. A review on this subject is presented by Pruppacher and Klett (2). There is general agreement that drop formation on small surface imperfections must be described as a nucleation process, the initial droplet being a cluster of perhaps only some 10 or 100 molecules. In those cases a relatively high saturation ratio is required for the formation of a macroscopic drop. On a clean surface the imperfections are expected to be small in number and small in size, consequently the critical saturation ratio is expected to be high.

The present study does not intend to contest the theory of heterogeneous nucleation but it attempts to explain why the actual critical saturation ratios for drop formation on hydrophobic surfaces are in general much lower than the values predicted by the nucleation theory. Suppose that on a real particle hydrophylic contaminations cover one percent of the surface. When these contaminations are large they may well be preferential sites of macroscopic drop formation before an adsorbed layer can grow to a critical thickness. But when the contaminations are small, heterogeneous nucleation can hardly interfere with drop formation from an adsorbed layer. In both cases the critical saturation ratio is relatively low.

On very small particles the size of the contamination can be of the same order of magnitude as the particle diameter. In that case drop formation may be dominated by hydrophylic contaminations on the particle. But even then the depression of the critical saturation ratio due to these contaminations is limited because the contamination is always smaller than the particle.

In an experiment by Liu *et al.* (9) condensation of water on a DOP aerosol has been studied. DOP (dioctyl phtalate) is a hydrophobic liquid on which $\theta > 40°$ for water. It is a stable compound with a low vapor pressure and it is available in a high grade of purity. The surface of the DOP droplets in this experiment can be assumed to resemble an ideal surface very closely; $\mathbf{r} \ll R$ and, with regard to Eq. [15], $S(\mathbf{r}) > S(R)$. For condensation of water on DOP particles it was found that $S_{\text{crit}} = 1.035$ for $R = 28$ nm and $S_{\text{crit}} = 1.12$ for $R = 9$ nm. These values coincide exactly with the theoretical values of $S(r)$ in Table II for $\theta = 0$, implying that water condenses on these oil drops just as readily as if they were water drops. Apparently the large contact angle for water on these oil drops is no impediment for condensation, contrary to the predictions of the classical theory of heterogeneous nucleation.

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