vapor phase by Volmer and Weber[9] and Becker and Doering[10] has to be modified only slightly to take into account the presence of the substrate. In essence, this model postulates that, in order to form a condensed phase from the supersaturated vapor, positive free-energy fluctuations are required to form stable aggregates of the condensed phase, thus introducing the necessity of overcoming an activation barrier (sometimes called the "nucleation barrier"). It is because of this barrier that a supersaturation greater than unity is required for condensation to take place.

(1) The Critical Nucleus The capillarity model predicts that the free energy of formation of a condensed aggregate goes through a maximum; i.e., the aggregate has a stability minimum with respect to dissociation into the vapor phase as it grows through its "critical" size. This maximum in free energy arises from the very large surface-to-volume ratio of the small aggregates, tending to decrease their stability, and the condensation energy, tending to increase it, as they grow in size.

To calculate the critical radius r^* of such an aggregate, we assume aggregates of surface area a_1r^2 exposed to the vapor phase, a contact area a_2r^2 between the aggregate and substrate, and a volume a_3r^3, where the a's are constants and r is the mean linear dimension of the aggregates. The total free energy of an aggregate with respect to dissociation into the vapor phase as a function of size is given by

$$\Delta G = a_3r^3\,\Delta G_v + a_1r^2\sigma_{v\text{-}c} + a_2r^2\sigma_{s\text{-}c} - a_2r^2\sigma_{s\text{-}v} \tag{3}$$

Here ΔG_v (negative) is the free energy of condensation of the film material in the bulk under the same conditions of supersaturation in ergs cm^{-3} and is given by

$$\Delta G_v = \frac{kT}{V}\ln\frac{R}{R_e(b)} \tag{4}$$

$\sigma_{v\text{-}c}$ (positive) and $\sigma_{s\text{-}c}$ (positive or negative) are the surface and interfacial (between deposit and substrate) free energies of the aggregate, respectively, and $\sigma_{s\text{-}v}$ is the surface energy of the substrate, all in ergs cm^{-2}. The $a_2r^2\sigma_{s\text{-}v}$ term enters into Eq. (3) because an area of free substrate surface equal to a_2r^2 disappears when the aggregate is created. The volume of one molecule of the film material is V, and $R_e(b)$ is the evaporation rate of monomers from the bulk at the substrate temperature. The ratio $R/R_e(b)$ is the supersaturation ratio.

Differentiating Eq. (3) with respect to aggregate size yields

$$\frac{\partial\Delta G}{\partial r} = 3a_3r^2\,\Delta G_v + 2a_1r\sigma_{v\text{-}c} + 2a_2r\sigma_{s\text{-}c} - 2a_2r\sigma_{s\text{-}v} \tag{5}$$

Here it is assumed that the shape of the aggregate does not change as its size changes, and also that ΔG_v, $\sigma_{v\text{-}c}$, and $\sigma_{s\text{-}c}$ do not change with size.

The free energy of the aggregate is a maximum for an aggregate of critical size, i.e., for $\partial\,\Delta G/\partial r = 0$:

$$r^* = \frac{-2(a_1\sigma_{v\text{-}c} + a_2\sigma_{s\text{-}c} - a_2\sigma_{s\text{-}v})}{3a_3\,\Delta G_v} \tag{6}$$

The free energy corresponding to this size is

$$\Delta G^* = \frac{4(a_1\sigma_{v\text{-}c} + a_2\sigma_{s\text{-}c} - a_2\sigma_{s\text{-}v})^3}{27a_3^2\,\Delta G_v^2} \tag{7}$$

The dependence of the free energy of an aggregate on its size is shown schematically in Fig. 1. The condition of maximum free energy corresponds to minimum stability of the aggregate, and occurs at the critical size r^*. For values of $r > r^*$, the r^3 term in Eq. (3) will predominate, leading to negative free energies and, therefore, stable aggregates for large radii. If an additional atom is added to an aggregate of critical size (called a critical nucleus), it becomes somewhat more stable and will, on the average, not dissociate into single atoms but will grow to form a larger, permanent island. If, on the other hand, an atom is taken away from the critical nucleus, it dissociates again. Therefore, in order to condense a permanent deposit, aggregates of critical size or larger have to be created first.

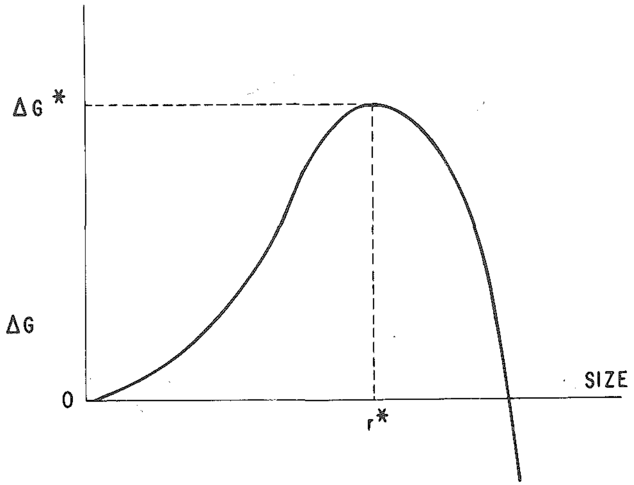

Fig. 1 The free energy of formation of an aggregate of film material as a function of size The aggregate has minimum stability at the critical radius r^*.

For a spherical cap nucleus of radius r, making a contact angle θ with the substrate, Eqs. (6) and (7) become, respectively,

$$r^* = \frac{-2\sigma_{v\text{-}c}}{\Delta G_v} \tag{6a}$$

$$\Delta G^* = \frac{4\pi\sigma^3_{v\text{-}c}}{3\,\Delta G_v^2}(2 + \cos\theta)(1 - \cos\theta) \tag{7a}$$

If the surface free energy of the nucleus is anisotropic, its shape will be a circular disk of height h. The number of monomers in a critical cluster is given by[8]

$$i^* = \frac{\pi h\sigma^2_{e\text{-}v}}{V(\Delta G_v + \Sigma\sigma/h)^2} \tag{6b}$$

where $\sigma_{e\text{-}v}$ = specific free-edge energy of the disk, and

$$\Sigma\sigma = \sigma_{c\text{-}v} + \sigma_{s\text{-}c} - \sigma_{s\text{-}v}$$

Equation (7) becomes, for the circular disk,

$$\Delta G^* = \frac{-\pi h\sigma^2_{v\text{-}c}}{\Delta G_v + \Sigma\sigma/h} \tag{7b}$$

(2) The Nucleation Rate Critical nuclei can grow to supercritical dimensions either by direct impingement and incorporation of atoms from the gas phase, or by collisions with adsorbed monomers diffusing over the surface of the substrate. If only a relatively small area of the substrate surface is covered by critical nuclei, the latter mechanism is probably the more important one, depending on the diffusion coefficient of the adsorbed monomers. For such a case, the rate at which critical nuclei grow is given by the number of initial nuclei per unit area, and the rate at which adsorbed monomers join it. Assuming a metastable equilibrium between the adsorbed monomers and aggregates of various sizes, one gets for the concentration of nuclei of critical size (neglecting small statistical mechanical corrections)

$$n^* = n_1\exp\left(\frac{-\Delta G^*}{kT}\right) \tag{8}$$