

### Clustering in adsorbed films

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Recently, Dash has shown that adsorption isotherms can show distinct types of behavior. In class I the bulk vapor pressure is reached asymptotically for an infinite adsorbed amount; in class II it is reached for a finite amount; in class III no adsorption takes place at all. We show that these possibilities can also be derived by a simple discussion of the possible forms of the free energy as function of the thickness of the adsorbed film. The question of clustering, i.e., the formation of drops, is also discussed.

In a recent paper, Dash<sup>1</sup> has developed a theory of clustering in adsorbed films, and described three classes of behavior, which correspond to three types of adsorption isotherm. In class I the saturated vapor pressure of bulk adsorbate is reached asymptotically as the thickness of the adsorbed layer becomes large; in class II it is reached at a finite thickness, and further adsorption is in clusters; in class III there is no adsorption at all.

The argument used in characterizing these classes makes strong use of the Young-Dupré wetting condition, which may not be familiar to some readers. The purpose of the present paper is to show how a large part of the results can be read off directly from the behavior of the free energy of the film as a function of thickness, and to connect the classification with this behavior. However, for the question of the clustering explicit reference to the wetting condition seems unavoidable.

Let  $F(n)$  be the free energy per unit area of a uniform adsorbed layer containing  $n$  atoms per unit area. Figure 1 illustrates the simplest possible shape for the  $F(n)$  curve; other shapes will be discussed later. In general  $F$  decreases monotonically with  $n$ , while the chemical potential

$$\mu = \frac{\partial F}{\partial n} \tag{1}$$

is negative and increases with  $n$ . The intercept with the  $F$  axis is the free energy per unit area of the bare substrate, i.e., it contains the surface free energy of the substrate, denoted by Dash by  $\gamma_{s0}$ . We may ignore the volume free energy of the substrate, which is a constant additive term for our purpose.

The chemical potential  $\mu$  is related to the vapor pressure  $p$ . If the vapor is a perfect monatomic gas, then

$$\mu = kT \left[ \ln(p/kT) - \frac{3}{2} \ln(mkT/2\pi\hbar^2) \right]. \tag{2}$$

In any event,  $\mu$  is a monotonically increasing func-

tion of the pressure.

For large  $n$ , the asymptotic form of  $F$  may be written

$$F_{\text{asym}} = n\mu_B(T) + \alpha_\infty(T), \tag{3}$$

where  $\mu_B$  is the bulk chemical potential, related to  $p_B$ , the saturated vapor pressure of bulk adsorbate.  $\alpha_\infty$  is the intercept of the asymptote with the  $F$  axis. From Eq. (3),  $\alpha_\infty$  is also the constant term in the asymptotic linear law, and therefore the surface free energy.

Since, for large  $n$ , our assumptions include a surface bounding the layer against the substrate, and another bounding it against the vapor,

$$\alpha_\infty = \gamma_{1s} + \gamma_{1v} \tag{4}$$

in the notation of Dash.<sup>1</sup>

For any other  $n$ , we can draw the tangent to the curve, and define the intercept with the  $F$  axis as  $\alpha(n)$ . Evidently

$$\alpha(n) = F(n) - n \frac{dF}{dn}, \tag{5}$$

and therefore

$$\frac{d\alpha}{dn} = -n \frac{d^2F}{dn^2}. \tag{6}$$

From (1) and (2),

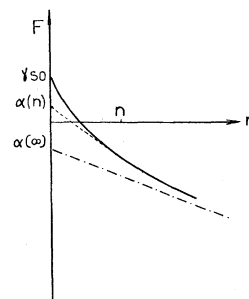


FIG. 1. Free energy vs coverage: class I. No point of inflection. Solid curve, uniform layer; dot-dashed line, asymptote.

$$\frac{d^2F}{dn^2} = \frac{d\mu}{dn} = kT \frac{d \ln p}{dn} \quad (7)$$

and (6) becomes

$$\frac{d\alpha(n)}{dn} = -nkT \frac{d \ln p}{dn}. \quad (8)$$

This is identical with the Gibbs equation for the spreading pressure  $\phi$ , except for the sign, so that

$$\phi(n) = -\alpha(n) + \text{const.}$$

But for  $n=0$ ,  $\phi$  vanishes, whereas  $\alpha$  is  $\gamma_{s0}$ . Hence

$$\alpha(n) = \gamma_{s0} - \phi(n). \quad (9)$$

Using Eq. (4) of Dash, we have

$$\alpha(n) = \gamma_{sv}. \quad (10)$$

From (4) therefore

$$\alpha_\infty - \alpha(n) = \gamma_{is} + \gamma_{iv} - \gamma_{sv}. \quad (11)$$

For the shape of the  $F(n)$  curve shown in Fig. 1, evidently  $\alpha_\infty < \alpha(n)$  for all  $n$ , and by (11) this means that the condition for complete wetting [Eq. (1) of Dash<sup>1</sup>] is satisfied for all  $n$ . Independently, inspection of Fig. 1 shows that, with increasing  $n$ ,  $\mu$ , and hence  $p$ , increases continuously to reach the bulk value asymptotically, corresponding to class-I behavior.

One may query whether the condition for complete wetting should have been seen as evidently necessary *a priori*, since its derivation assumes the coexistence of the film with a liquid phase, which does not exist below bulk vapor pressure. The present derivation, which does not make use of the wetting condition, confirms that it is satisfied in class-I systems.

The alternative situation, in which  $\alpha_\infty > \alpha(n)$ , requires that the  $F(n)$  curve have somewhere a negative curvature, either by having a point of inflection as in Fig. 2, or negative curvature all the way, as in Fig. 3.

First consider the case of Fig. 2. Here there exists a value  $n_1$  of the coverage, for which the tangent is parallel to the asymptote. Uniform layers between 0 and  $n_1$  are still stable, and the vapor pressure rises with  $n$  to reach the bulk value at  $n_1$ . Beyond  $n_1$ , the uniform layer, whose free energy would be given by the broken curve, is unstable, because its free energy is above the double line, which for  $n > n_1$  represents an adsorbed layer with  $n_1$  atoms, with  $n - n_1$  in bulk form. (We need not attribute any surface free energy to the latter, since we are concerned with the limit of a very large area of substrate, whereas the nonadsorbed substance could be in a single drop, and its surface area negligible.)

It follows that in this case there cannot be a uni-

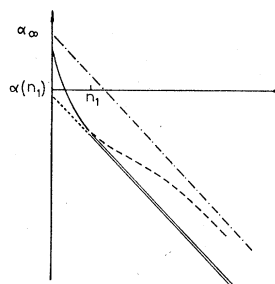


FIG. 2. As Fig. 1, but with one point of inflection; class II. Dashed curve, unstable uniform layer; double line, some bulk adsorbate.

form layer with a coverage exceeding  $n_1$ . The diagram does not tell us directly anything about the stability of a nonuniform layer. However, at and above  $n_1$  the system is at the bulk vapor pressure, and we can apply macroscopic considerations to a nonuniform configuration, such as a large single drop adhering to the surface, on top of the uniform layer.

In that case we can impose the setting condition

$$\gamma_{vi} \cos \theta + \gamma_{is} - \gamma_{sv} = 0, \quad (12)$$

where  $\theta$  is the angle of contact. The requirement that  $\cos \theta$  lie between 1 and  $-1$  leads, in conjunction with (11), to the conditions

$$-2\gamma_{sv} < \alpha(n_1) - \alpha_\infty < 0 \quad (13)$$

If the curve is as in Fig. 2, the second of these inequalities is satisfied, since the tangent at  $n_1$  lies below the asymptote. Hence  $\cos \theta$  is less than unity, and we do not have complete wetting, in agreement with our conclusion that no uniform accretion can take place. Whether the first part of (13) is satisfied, depends on the value of  $\gamma_{sv}$ . If this is large enough, there exists a value of  $\theta$  satisfying (12), and a drop can adhere to the surface. If  $\gamma_{sv}$  is too small, there is no possible value for  $\theta$ , and no further adsorption, uniform or otherwise, can take place.

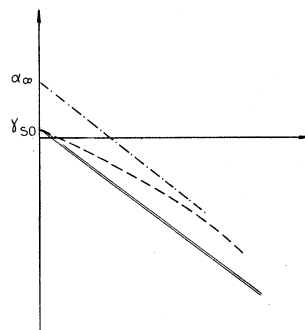


FIG. 3. As Fig. 2, but with negative initial curvature; class III.

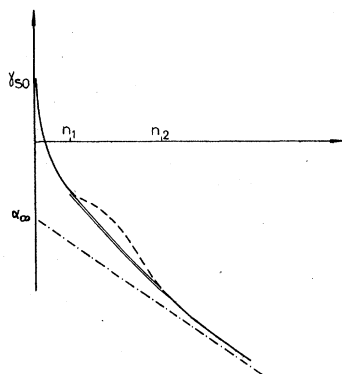


FIG. 4. As Fig. 1, but with two points of inflection. Double line, two-phase region.

In either case, the adsorption isotherm resembles that deduced by Dash for his class II. If the first part of (13) is satisfied, adsorbate added beyond  $n_1$  will form a drop or drops on top of the uniform layer. Otherwise no more adsorbate adheres to the surface, but it will condense anywhere (not excluding the possibility of drops resting on, but not wetting, the film-covered surface). We shall refer to these two possibilities as classes IIa and IIb. They may not be easy to distinguish experimentally.

In the case illustrated in Fig. 3, in which the  $F(n)$  curve has negative curvature from the beginning, no uniform film can form at all. The whole of the curve lies above the line through its starting point parallel to the asymptote. Thus bulk liquid is more stable than any uniform layer. Here again, the second part of (13) is necessarily violated at  $n=0$ . If the first part is still satisfied there, i.e., for sufficiently large  $\gamma_{sv}$ , there will be a finite wetting angle, and a drop may form on the substrate. Otherwise no adsorption can take place at all. We shall denote these two situations by IIIa and IIIb, respectively. Again the observed isotherms look the same, and have the form given by Dash for class III. His description seems to fit

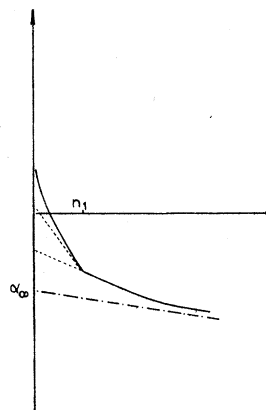


FIG. 5. As Fig. 1, but with a discontinuous rise in pressure.

our class IIIb.

Other possible shapes include a curve with two points of inflection, as in Fig. 4. The curve sketched there has a common tangent, with contacts at  $n_1$  and  $n_2$ . The part of the curve between these points is now unstable, and replaced by the tangent, representing a two-phase region with part of the surface having coverage  $n_1$  and the rest having  $n_2$ . Beyond  $n_2$  the vapor pressure, which is constant from  $n_1$  to  $n_2$ , rises again, to reach the bulk value asymptotically.

The examples discussed so far have a chemical potential which is a continuous function of the coverage. One cannot rule out *a priori* the possibility of discontinuities in  $\mu$ , hence of breaks in the slope of  $F$ . An example is shown in Fig. 5, where there is a kink at  $n_1$ . Here, as the coverage increases through  $n_1$ , the chemical potential increases discontinuously. This, ideally, is the behavior upon completion of a monolayer at  $T=0$ . For real systems, and at finite temperature, there will always be some rounding off.

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<sup>1</sup>J. G. Dash, Phys. Rev. B 15, 3136 (1977).